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Surfactant-induced relative permeability modifications for oil recovery enhancement

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SURFACTANT-INDUCED RELATIVE PERMEABILITY MODIFICATIONS FOR OIL RECOVERY ENHANCEMENT

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DEDICATION

This work is dedicated to my professor and to my beloved family…

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NOMENCLATURE

N_{ca} = Capillary Number

ν = Velocity

μ = Viscosity

σ = Interfacial tension

θ = Contact angle

ϕ = Porosity

ΔP_h = pressure drop gradient

A = area

L = length

q = flow rate

K = absolute permeability

K_e = effective permeability

K_r = relative permeability

δ_w = wettability index to water

V_{osp} = oil volume displaced by spontaneous water imbibition

V_{ot} = the total oil volume displaced by both spontaneous imbibition and centrifugal (forced) displacements of water

δ_o = wettability index to oil

V_{wsp} = water volume displaced by spontaneous oil imbibition alone

V_{wt} = total water volume displaced by both spontaneous imbibition and centrifugal (forced) displacements of oil

I = Amott-Harvey relative displacement index

W = USBM wettability index

A_1 = area under the capillary pressure versus saturation curve obtained during oil drive

A_2 = area under the capillary pressure versus saturation curve obtained during brine drive

S_{wi} = Initial water saturation

S_{or} = Residual oil saturation

K_{ro} = end-point relative permeability to oil at S_{wi}

K_{rw} = end-point relative permeability to water at S_{or}

$e_{o,}$ e_w = Corey exponents

h = thickness

B_o = oil formation volume factor

E_D = microscopic displacement efficiency

E_V = volumetric sweep efficiency (macroscopic displacement efficiency)

E = overall efficiency

ABSTRACT

Surfactants have been considered for enhanced oil recovery by reduced oil-water interfacial tension. However, these surfactants may enhance oil recovery via wettability alteration as well. This study experimentally determines the influence of surfactant type and concentration on oil recovery, oil-water relative permeabilities and wettability in reservoir rocks. Several coreflood experiments were conducted using Yates reservoir fluids in Berea rocks and two types of surfactants (nonionic and anionic) in varying concentrations. A coreflood simulator was used to calculate oil-water relative permeabilities by history matching recovery and pressure drop measured during the corefloods. These relative permeability variations were interpreted using Craig's rules-of-thumb to characterize wettability alterations induced by the surfactants.

The two main mechanisms behind the use of surfactants to enhance oil recovery are (1) reduction in interfacial tension and (2) alteration of wettability. To discern the relative contributions from these two mechanisms on enhanced oil recovery, two series of coreflood experiments have been conducted using a nonionic surfactant in varying concentrations. The first series used decane as the oil phase to quantify the effect of reduction in interfacial tension on oil recovery, while considering wettability effects in the decane-brine-Berea system to be negligible. The second series used Yates crude oil in place of decane to quantify the effects of reduction in interfacial tension as well as wettability alteration on enhanced oil recovery. The same two sets of experiments are then repeated with the anionic surfactant. The comparison of results of these four sets of experiments showed significantly higher oil recoveries for second series of experiments,

indicating that the surfactants have altered wettability. The optimum surfactant concentration was found to be 3500 ppm.

In three of the four cases studied, oil/water emulsions caused high pressure drops during the flooding experiments, strongly affecting the relative permeability curves. Craig's rules-of-thumb may not be applicable in systems containing emulsions. This study suggests that the development of a mixed-wettability state yields significantly higher oil recoveries observed in Yates crude oil systems. The significant contributions of this study are the quantification of the wettability altering capability of surfactants and the consequent enhancement of oil recovery.

CHAPTER 1

INTRODUCTION

1.1 Background

Crude oil makes a major contribution to the world economy today. The provision of heat, light and transport depends on oil and there has not been a single energy source to replace crude oil so far that has broadly integrated. To meet the rising energy consumption in the world, there is a dire need to produce more crude oil. Stagnant oil production and unimpressive recovery by conventional methods have made the situation more precarious. Hence, attention is being paid to Enhanced Oil Recovery (EOR) techniques for recovering more oil from the existing oilfields.

On an average, only about a third of the original oil in place can be recovered by the primary and secondary recovery processes. The rest of oil is trapped in reservoir pores due to surface and interfacial forces. This trapped oil to secondary water floods can be recovered by reducing the capillary forces that prevent oil from flowing within the pores of reservoir rock and into the well bore. More and more advanced technologies are being implemented in the oil industry today to recover this trapped oil under the banner called " Enhanced Oil Recovery Processes". Any process that involves the injection of a fluid or fluids into a reservoir to supplement the natural energy present in a reservoir, where the injected fluids interact with the reservoir rock/oil/brine system to create favorable conditions for maximum oil recovery is known as an EOR process[1]. These favorable interactions intended to maximize oil recovery may be oil swelling, lowering of IFT, rock wettability modification, oil viscosity reduction and favorable phase behavior[1].

The effect of capillary forces on trapping of oil with in the pores of reservoir rock is normally generalized by the use of a dimensionless number, called the capillary number. The capillary number is defined as the ratio of viscous to capillary forces.

$$N_{ca} = \frac{ViscousForces}{CapillaryForces} = \frac{v\mu}{\sigma \cos\theta} \qquad \text{---------- (1)}$$

Where v and μ are the velocity and viscosity, respectively of the displacing fluid, σ is the oil-water interfacial tension and θ is the contact angle.

The discovered original oil in place in the U.S is 536 Billion barrels, out of which 162 billion barrels of oil has been recovered by 1993. However, 23 billion barrels of oil can be recovered economically through the application of current proven technology. Therefore, there still remains 351 billion barrels of oil trapped inside the producing reservoirs, which amounts to nearly two thirds of original oil in place. The worldwide target for EOR is estimated to be two trillion barrels. Hence, EOR processes are essential to recover these huge amounts of trapped oil.

The following flow sheet shows the types of various EOR processes that are currently employed in the oil industry.

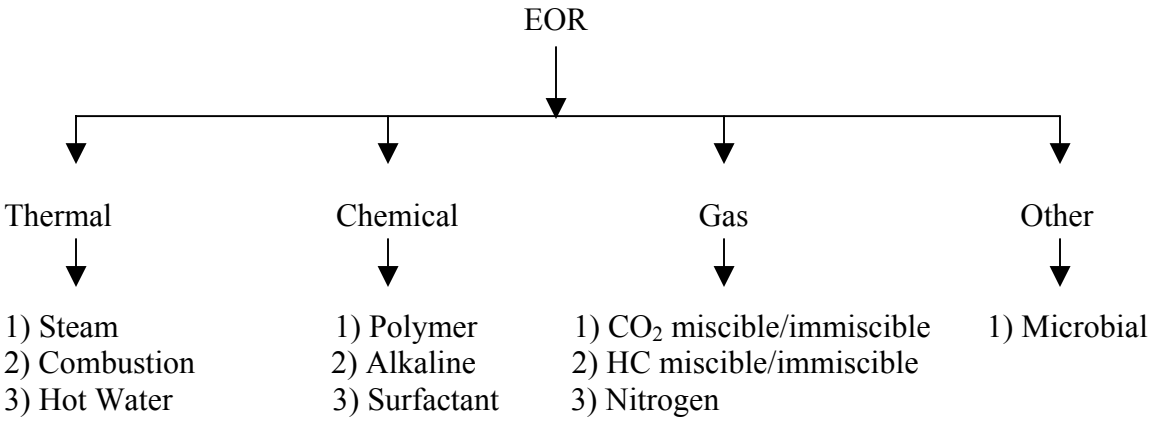


Figure 1: Flow Sheet for EOR Processes

1.2 Objective

The effect of capillary number on residual oil saturation (Klins[2]) shows that an increase of four to five orders of magnitude in capillary number is required in any EOR process in order to reduce the residual oil saturation significantly. From Eq.1, it is understood that the capillary number can be increased by either reducing the interfacial tension (σ) or by letting the value of contact angle (θ) approach 90^0, which means an intermediate wettability of the rock-fluids system. Most of the previous work done in this area has ignored the contact angle term in the above equation by setting $\cos\theta = 1.0$ (or $\theta = 0^0$). This is equivalent to assuming perfect water-wet conditions in all reservoirs. It should be noted here that there are more non water-wet reservoirs than water-wet ones (Anderson[3]). Therefore, the main objective of this work is to study the effect of wettability alteration on oil recovery enhancement by the use of low cost surfactants.

An attempt is made in this project to investigate the effect of surfactants on enhanced oil recovery. The use of surfactants has long been considered in oil industry for enhanced oil recovery through reduction in oil-water interfacial tension. However, the large reduction in interfacial tension required for this mechanism is usually too expensive to be economical. Furthermore, the potential capability of these surfactants to enhance oil recovery through wettability alteration remains largely unexplored. This study will experimentally determine the influence of surfactant type and concentration on oil recovery and wettability alteration as quantified by oil-water relative permeabilities.

1.3 Methodology

Several coreflooding experiments were conducted in the present study to examine the effect of surfactants on wettability and oil recovery. We used Yates reservoir fluids and decane in Berea sandstone, two types of surfactants- nonionic (ethoxy alcohol) and anionic (ethoxy sulphate) in varying concentrations. A coreflood simulator was used to calculate oil-water relative permeabilities by history matching the recovery and pressure drop data from the corefloods. Later, these relative permeability variations have been interpreted using Craig's rules-of-thumb[71] to characterize wettability alterations induced by the surfactants.

Two series of coreflood experiments were conducted using a nonionic surfactant in varying concentrations. The first series used decane as the oil phase to quantify the effect of only the reduction in interfacial tension on oil recovery, since wettability effects in the decane-brine-Berea system are considered to be negligible. The second series used crude oil (from the Yates field in West Texas) in place of decane to quantify the effects of reduction in interfacial tension as well as wettability alteration on enhanced oil recovery. Next, the same two series of experiments were repeated using an anionic surfactant at different concentrations. Finally, the results from these four series of coreflooding experiments using two types of surfactants in varying concentrations were utilized to analyze the effects of surfactant type and concentration on oil recovery, oil-water relative permeabilities and wettability. Thus the significant contributions of this study are the experimental proof for the concept of wettability alteration by the use of surfactants, the quantification of the extent of wettability shifts and the consequent enhancement in oil recovery.

CHAPTER 2

LITERATURE REVIEW

This project focuses on enhancement of oil recovery in a fractured reservoir through surfactant-induced relative permeability modifications. Therefore, the related literature is thoroughly reviewed and reported in the following sections.

2.1 Yates Reservoir Characteristics

Yates field, located 90 miles south of Midland, Texas was discovered in 1926. The main reservoir is the San Andres Carbonate, which is a naturally fractured dolomite reservoir. The Yates field structure is a broad and gentle (1^0 to 4^0) asymmetric, horseshoe-shaped anticline with greater than 400 ft of closure over 26,400 acres at the San Andres stratagraphic level. There are more than 1500 wells with approximately 10 acre spacing, although the active current well count is less than 500. Cumulative production from this field through 1999 is over 1.3 billion barrels of oil.

Until 1976 the field was operated under depletion, producing mainly from the fractured Grayburg and San Andres formations. As the pressure depleted, free gas evolved and rapidly escaped through the fractures to form a gas cap at the top. A gas injection pressure maintenance program was started in 1976 to retard the water invasion into the oil-producing zone. The gas cap gravity drainage mechanism has been an effective recovery mechanism in the Yates field. Several improved oil recovery pilots such as “Wettability Alteration of Reservoirs Using Surfactant (WALRUS)“ and “Thermally Assisted Gravity Segration (TAGS)” are underway to enhance oil production from this field.

Reservoir rock and fluid properties[4]:

Reservoir temperature : 82^{o}F

Rock type : Dolomite

Permeability : 100 md (on average)

Porosity : 15 % (on average)

Wettability : Oil-wet

Fracture[4]:

Porosity : 2%

Permeabilty : > 1 Darcy

Yates stocktank crude oil[4]:

Viscosity : 12.8 cp

Density : 0.874 g/cc

Yates synthetic brine[4]:

Crude oil/brine IFT : 50 dynes/cm

2.2 Fracture/Matrix Mass Transfer

Oil production from fractured reservoirs normally occur by spontaneous water imbibition and oil expulsion from the matrix into fracture network. Hence, spontaneous imbibition is considered to be the most important phenomenon in oil recovery from fractured reservoirs. In fractured systems, the rate of mass transfer between the rock matrix and fractures usually determines the oil production. Matrix contains most of the oil due to its much higher storage capacity compared to the fracture network. So, an effective matrix-fracture interaction is required to recover the matrix oil. For water-wet reservoirs, having sufficient supply of water in the fractures, the matrix oil is recovered

mostly by capillary imbibition where simply the capillary suction draws the wetting liquid into the matrix. Thus, fractured reservoirs are amenable to waterflooding only if the matrix blocks are water-wet. Further, injection of dilute surfactant in a water-wet reservoir can recover additional oil by lowering oil/water interfacial tension or wettability alteration. So, the emphasis here is transporting the surfactants through the fractures into the rock matrix where the residual oil to water flood resides.

However, if the reservoir is oil or intermediate-wet, then waterflood recovers the oil only from the fractures and completely bypasses the matrix blocks. Injection of high pressure gases have been considered for oil recovery from such fractured reservoirs. These displacements are conducted at adverse viscosity ratio and non-zero density difference. In a fractured reservoir, oil will tend to be bypassed in the matrix blocks and in some fractures due to viscous fingering and gravity override. The recovery of this bypassed oil depends upon the level of mass transfer with the injectant. Generally, the mass transfer mechanisms that occur between the matrix and the fracture can be categorized into three types: transport within a single phase, transport across a partially immiscible phase along a single tie-line and transport across partially immiscible phases across many tie-lines (lines joining equilibrium liquid and vapor compositions of hydrocarbon components). Diffusion and dispersion mechanisms are important in all the cases. Equilibrium constants and phase behavior are important in the last two cases. Capillarity is important in the last two cases whereas insignificant in the first case. Gas injection is considered to be the main mechanism for oil recovery in oil and intermediate-wet fractured reservoirs as it allows to recover substantial quantities of oil trapped in the matrix. The main mechanism involved in this recovery process is the

gravity drainage. The density difference between the gas in the fracture and the oil in the matrix causes the oil production until gravitational forces are balanced by the capillary retaining forces.

Romm[5] measured the two-phase flow behavior and oil-water relative permeabilities in a single fracture and obtained straight-line relative permeabilities for the phases as a function of wetting phase saturation for smooth fracture surface.

Tsang[6] studied the effect of tortuosity on single-phase flow in a single fracture using statistical correlations. It was found that the more small apertures there are in the aperture distribution, the larger is the effect of tortuosity. When the fraction of the contact area between the fracture surfaces was raised to 30%, the aperture distributions were invariably large at small apertures and the effect of fracture roughness and flow path tortuosity depressed flow rate from the value predicted by the parallel plate representation of a fracture by three or more orders of magnitude.

Wang and Narasimhan[7] conducted studies to characterize the fracture apertures and they created fracture surface roughness using fractal geometry correlations. They developed a fractal fracture model through the use of variograms to relate the aperture correlation structure with physically meaningful shear displacement and mathematically interesting fractal geometry to characterize rough fractures.

Pruess and Tsang[8] experimentally measured the two-phase gas-water relative permeabilities for a single fracture. They verified the results numerically by assigning log normally distributed apertures while neglecting the matrix contribution.

Mattx and Kyte[9] studied the effects of matrix block size on the recovery for reservoir scaling purposes. They showed that the imbibition time required to recover a given fraction of oil from a single matrix block is proportional to the square of the distance between fractures. They also observed that the recovery is sensitive to injection rate.

Iffly et al.[10] studied both experimentally and numerically the effect of petrophysical and lithological characteristics on the imbibition behavior for a single matrix block with different imbibition conditions. They also examined the effect of water composition on imbibition. The results showed that physico-chemical bondings between connate water, injected brine, oil and rock at any time during the imbibition can alter oil recovery. Organic molecules can influence oil recovery by changing $\sigma\cos\theta$ alone.

Graham et al.[11] studied the effect of fracture flow rate on the matrix imbibition. They found that imbibition is sensitive to injection rate and proportional to the square root of the matrix permeability, interfacial tension, a function of contact angle and depends on the fluid viscosities and characteristics of the rock.

Braester[12] analytically modeled simultaneous flow of two immiscible fluids in a fractured reservoir and found saturation shock in the fractures, whereas in the blocks saturation varied gradually. In contrast to the Buckley-Leverett solution for a non-fissured porous medium, the front velocity and the saturation at the front decreased with time because of transfer of wetting fluid from fissures to the matrix blocks. The results were found to be in agreement with laboratory experiments and field observations.

Kleppe and Morse[13] conducted laboratory experiments involving flow of oil and water on matrix blocks surrounded by fractures and used a numerical model to simulate the experimental results. They found that the ultimate oil recovery from fractured

reservoirs is greatly affected by the production rates at conductivity ratios higher than 1. For fracture flow capacities of the order of $1/10^{th}$ matrix flow capacities, the effect of production rate on oil recovery is negligible. At the production rates of the order of 0.05 times the gravity reference rate, fractured systems behave essentially as non-fractured reservoirs.

Kazemi et al.[15] have demonstrated that the modeling approach taken by de Swaan[14] is more convenient and accurate than the frequently used dual porosity approach for simulation of flow through a fractured reservoir. De Swann[13] and Kazemi et al.[15] neglected capillary pressure and used an analytical solution to test their finite difference numerical solution. A comparison of the numerical and analytical solutions revealed that the finite difference solution had numerical dispersion problems even if very small time and spatial increments are used.

Civan[16,17] extended the approach of de Swann[14] to include compressibility, gravity and capillary pressure and obtained an efficient numerical solution using differential quadrature. Civan[18,19] has shown that quadrature and cubature methods can alleviate numerical dispersion even for 10 times greater spatial increments and 3000 times larger time steps than the finite difference solution.

Gupta et al.[20] extended the double exponent model proposed by Civan[16,17] to include the contribution of dead-end pore-space in the matrix to the oil recovery. Inclusion of contact angle term in the time scaling group of their model improved correlation of the imbibition recovery for samples with varying shapes and sizes, flow boundary conditions and fluid and rock properties They used triple exponential functions to analyze their experimental data. These terms represent the transfer of oil from (1) dead-end pores to

the primary network of interconnected pores (2) from the primary network to the matrix-fracture interface and (3) from the interface to the fracture system. This model improved matches between experimental and predicted oil recovery during imbibition compared to the previous models.

Gupta et al.[21] also investigated the effect of matrix-fracture transfer on oil displacement by water imbibition in naturally fractured porous media if wettability and process rate vary. They developed a mathematical model coupling the two-phase flow in the fracture network and in the porous matrix. An oil-water exchange function incorporates the rates of transfer of oil from the dead-end pores to the network of pores and then to the network of fractures. Parametric studies with this model indicated that the rate constants and matrix wettability play important roles in accurate description of oil recovery during waterflooding in naturally fractured reservoirs.

Thus, by referring to the latest previously published literature on fracture-matrix mass transfer, it can be concluded that the wettability plays a vital role in accurately predicting the mass transfer flow behavior between the matrix and fracture in a fractured reservoir.

2.3 Surfactants

A surfactant is a polar compound, consisting of an amphiphilic molecule, with a hydrophilic part (anionic, cationic, amphoteric or nonionic) and a hydrophobic part. Addition of surfactant to oil–water mixtures reduces interfacial tension and/or alters wettability.

Depending upon the nature of the hydrophilic group, the surfactants are classified as:

1. Anionic - the surface-active portion of the molecule bears a negative charge (e.g., $RC_6H_4SO_3^-Na^+$, alkyl benzene sulphonates).

2. Cationic - the surface-active portion bears a positive charge (e.g., $RNH_3^+Cl^-$, salt of a long chain amine).
3. Amphoteric (or) zwitterionic - both positive and negative charges may be present in the surface-active portion (e.g., $RN^+H_2CH_2COO^-$, long chain amino acid).
4. Nonionic - the surface-active portion bears no apparent ionic charge (e.g., $RCOOCH_2CHOHCH_2OH$, monoglyceride of long chain fatty acid).

When a surfactant is injected, it disperses into oil and water and lowers interfacial tension thereby increasing the capillary number. As a result, more of the otherwise immobile oil becomes mobile. At the same time, an oil-in-water emulsion may form, blocking the larger pores. This often leads to an improvement in the effective mobility ratio. The injected surfactant continues to mobilize oil and bank it up until the surfactant is diluted or otherwise lost due to adsorption by the rock until it is no longer available to lower the interfacial tension and mobilize oil. At that point, the process degenerates into a water flood.

The capillary pressure resistance to flow is proportional to oil/water interfacial tension divided by the diameter of the constriction. Viscous forces due to pressure gradients in the reservoir are much lower than the capillary forces. Oil mobilization is achieved if the capillary number is increased. Viscous forces cannot be increased greatly because of the limited pressure resistance of the reservoir. Hence, the reduction of the interfacial tension by the use of surfactants could produce the desired effect.

However, for significant enhancements in oil recovery, several orders of magnitude reduction in interfacial tension is required. The surfactants capable of generating this reduction are expensive and are required in large quantities, rendering

them uneconomical for field application. Hence, our emphasis is to study the wettability alteration rather than reduction in oil-water interfacial tension. Wettability alteration can be induced by low cost surfactants at moderate concentrations.

Factors that affect the interaction of surfactants with the solid surface of porous rock and consequently affect wettability are: surfactant structure, surfactant concentration, kinetics, pore surface composition, surfactant stability, cosurfactants, electrolytes, pH and temperature, pore structure/surface roughness and reservoir type and characteristics. Surfactant adsorption at the solid-liquid interface is a necessary but not sufficient condition for wettability alteration. A number of studies have shown that wettability shifts from oil-wetting toward water-wetting due to surfactant adsorption.

- **Surfactant Structure[22]:** Surfactants are amphipolar or amphipathic molecules composed of a hydrophilic head and a hydrophobic tail. This dual nature of surfactant produces a strong affinity for interfaces between the immiscible fluids such as oil and water. The surfactant by adsorbing on a fluid/solid interface reduces the interfacial tension and thereby alters the wettability of the surface. A surfactant that orients itself on a surface in such a way that the surfactant molecules have the hydrophobic tail groups away from the surface or along the surface will decrease water-wetting and increase oil-wetting. Similarly, the orientation of a surfactant with the head group away from the surface can make the surface more water-wet.
- **Surfactant Concentration[22]:** When the surfactant concentration in a solution is kept below its critical micelle concentration (CMC), the surfactant will be composed of monomers. At concentrations above CMC, surfactant micelles are

formed and the monomer concentration remains relatively constant with increasing surfactant concentration. The surfactant adsorption follows Langmuir isotherms. At low concentrations, the hydrophobic tail group of the surfactant is close or parallel to the surface and the hydrophilic head group is oriented toward water. As the surfactant adsorption increases, the surfactant molecules become more perpendicular to the surface until the CMC is reached where the surface is saturated. This difference in the orientations of the surfactant molecules changes the surface from oil-wet at low concentrations to water-wet at CMC and higher concentrations.

- **Kinetics[22]:** In reservoirs, surfactants must be transported through the pore networks by an injected fluid phase, usually water. The wettability alteration by the surfactants is related to surfactant diffusion and adsorption rates. If the diffusion rate or adsorption rate for the surfactant is slow relative to the creation of new water-rock interfaces, then the wettability of the pore surfaces may vary with time. These non-equilibrium effects are not understood and may affect the oil displacement in porous rocks.
- **Pore Surface Composition[22]:** Most reservoir formations are composed of mixtures of silica, clays, limestone and dolomite. Based on the normally water-wet tendency of the silica based matrix components, it is often assumed that most reservoirs are water-wet. However, Anderson[3] reported that there are more non water-wet reservoirs than water-wet ones through laboratory evaluation of contact angles of different oil producing reservoirs from various areas of the world. The factor that masked the water-wet character of bulk rock compositions in most

reservoir formations was the formation of films on the pore surfaces that resulted from the deposition of crude oil components and/or original organic films. The result of the varied composition on reservoir pore surfaces is that surfactants can interact with these surfaces at the pore level and alter the original wettability.

- **Surfactant Stability[22]:** Normally a long period of time is needed to transport surfactants through reservoir pore network and alter the wettability of the pore surfaces. The surfactant must maintain its chemical structure and interfacial properties. The stability of surfactants at reservoir temperatures in appropriate brine can be determined from cloud point and interfacial tension measurements in the lab.
- **Cosurfactants[22]:** Cosurfactants added to a surfactant can interact with the surfactant in solution to improve its behavioral characteristics. Some alcohols can reduce the interfacial tension. Binary mixtures of surfactants such as anionic and nonionic can reduce the surfactant adsorption[23].
- **Electrolytes and pH[22]:** Electrolytes and pH influence the rock pore surface interaction with the surfactant. Electrolytes affect the solubility of surfactants[24]. The effects of pH ($2 < pH < 12$) on advancing and receding contact angles for anionic and cationic surfactants were measured by Zorin et al.[25] in 0.1 N Nacl brine on polished quartz surfaces. Both the advancing and receding contact angles decrease with increasing pH. No hysteresis was observed with the anionic surfactant. However, substantial hysteresis was observed for advancing and receding contact angles with the cationic surfactant.

- **Temperature:** Temperature influences the wettability alteration by affecting either the surfactant or the surfactant-surface adsorption characteristics. Ziegler et al.[26] observed a decrease in the adsorption of nonionic surfactant with the increase of temperature at low surfactant concentrations, while the converse was true at high concentrations. For Noll et al.[24], similar results were obtained for anionic and cationic surfactants regardless of surface wettability.
- **Pore Surface Roughness[22]:** Pore surface roughness affects the apparent wettability induced by surfactants in the same way as the surface roughness affects the equilibrium or advancing and receding contact angles. Vijapurapu et al.[27] investigated the effect of surface roughness on equilibrium advancing and receding contact angles using different solid substrates and Yates reservoir fluids. The water-advancing contact angles on silica-based surfaces declined sharply with increasing surface roughness, indicating a shift from oil-wet on smooth surfaces to either intermediate-wet or weakly water-wet on rougher surfaces. Dolomite and calcite surfaces displayed only a slight decline in advancing contact angle with roughness and remained oil-wet within the range of roughness examined. The receding contact angles on all the solid substrates indicated insensitivity to surface type and roughness.
- **Reservoir Characteristics[22]:** The wettability alteration of a reservoir by surfactants is dependent on reservoir features. The sweep efficiency of reservoir influences the quantity of surfactant that contacts the reservoir rock matrix. In a highly fractured reservoir where the oil displacement is capillary dominated, the surfactant will be transported mostly by the spontaneous imbibition of water into

the rock matrix. At lower surfactant concentrations, the quantity of surfactant may not be sufficient to adsorb on the rock matrix, but it may be sufficient to alter the wettability of the portions of the pore surfaces that were first encountered. For viscous-dominated oil displacement, most of the surfactant is transported through the high permeability zones of the reservoir as water flows through the reservoir matrix. Even at low surfactant concentrations, the quantity of surfactant may satisfy matrix adsorption if sufficient surfactant is injected. Hence, the adsorption of the surfactant is controlled mainly by the concentration of the surfactant, its dilution by formation water and the water volume displaced through the matrix.

The use of surfactants in enhanced oil recovery has been reviewed by Shah and Bansal et al.[28]. Mattax et al.[29] studied surfactant behavior in carbonate rocks and concluded that surfactants have limited application in carbonate reservoirs due to fractures, low matrix permeability, dead end pore volume, high hardness, salinity, heterogeneity and adsorption. Krumrine[30] examined surfactant use in sandstones. Holestein[31] studied the effect of salinity and temperature on the use of surfactants and reported that over 75% of reservoirs were unsuited to current surfactant formulations (sulfonates) because of high salinity or temperature. He set the salinity limit at 4 - 5.5% for conventional surfactant formulations.

Boneau and Clampitt et al.[32] conducted coreflood experiments both in oil-wet and water-wet sandstones of similar permeability, porosity and pore structure using a surfactant and found that the tertiary oil recoveries ranged from 55 to 65% in oil-wet sandstones and 90 to 95% in water-wet sandstones. The surfactant system displaced less oil from the highly oil-wet sandstone because there was three to five times more sulfonate

adsorption in oil-wet sandstone than in water-wet sandstone. They did not investigate the effect of either interfacial tension or wettability alteration on oil recovery. Based on these experiments, they recommended an aqueous surfactant system (5.0 wt% petroleum sulfonate, 3.0% isobutyl alcohol and 92% brine) for the oil-wet sand stone of the North Burbank Unit.

Trogus et al.[33] studied the adsorption of anionic and nonionic surfactants on sandstones and found that the adsorption isotherms were Langmuir. The adsorption levels for both anionics and nonionics are of comparable magnitude. Adsorption increases sharply as concentration increases and then levels off at the critical micelle concentration for anionic and nonionic surfactants. The adsorption decreases with the increasing molecular weight for nonionics and the opposite is true for anionics. Negligible adsorption was observed for anionics containing sulfonates with an alkyl chain length of 9 or less.

Lawson[34] studied adsorption of both nonionic and cationic surfactants on sandstones and carbonates. For nonionic surfactants, the adsorption on sand stone was high and is relatively insensitive to solution salinity. Adsorption on carbonates was lower than on sandstone. For anionic surfactants, they found that adsorption isotherms were Langmiurian and multivalent cations were found to increase the adsorption. Salts of large anions and common detergent builders such as $Na_2B_4O_7.10H_2O$, $Na_5P_3O_{10}$ and Na_3PO_4 reduce the adsorption of anionic surfactants.

Stournas[35] discovered a new class of surfactant amphoteric, which incorporates both an anionic and a cationic center in the same molecule and found that these surfactants are chemically and thermally stable and do not precipitate in the presence of

monovalent and/or divalent cations. These surfactants can lower the oil-water interfacial tension to millidyne region in the presence of over 200,000 ppm of total dissolved solids. However, they did not investigate the alterations in wettability caused by these surfactants.

Chou et al.[36] investigated a new class of surfactants (oligomeric) when used as cosurfactant in a surfactant formulation. When used at a concentration about one-tenth of active surfactants, the formulation had higher solubilization capacity, lower interfacial tension, higher optimal salinity, higher salt tolerance, higher viscosity and lower adsorption loss. These benefits may improve the economics of surfactant flooding and broaden its application range.

Bakes et al.[37] studied the applicability of surfactants at various temperatures, pH, ionic concentrations and surfactant concentrations in fractured carbonate reservoirs. They reported that the primary criteria for surfactant selection were the formation of stable phases, absence of emulsions or precipitates and development of low interfacial tension. They screened the surfactants for low concentrations that would make them suitable for continuous waterfloods. They have tested available commercial and research surfactants such as cationic, anionic, nonionic and amphoteric and concluded that none of them is successful because of unsatisfactory phase behavior or insufficient reduction of interfacial tension.

Ballard et al.[38] investigated the influence of the surfactant concentration (sulphonates, fatty acids and fatty acid amino derivatives) in oil-based mud filtrates on wettability alteration of glass surfaces. Their contact angle measurements showed that the

surfactants in oil-based mud filtrates adsorb on to silica surfaces to build a monolayer, thus changing the initially strongly water-wet surface to one of intermediate wetting.

Menezes et al.[39] studied cationic and anionic surfactants used in drilling muds and completion fluids on wettability alteration in sandstones and carbonates. They found that a structural component is needed in addition to van Der Wall's and electrostatic components to calculate a theoretical contact angle that is comparable with the experimental angle. The structural component varies with the concentration of the surfactant due to the formation of monolayer and bilayer structures.

Mannhardt et al.[40] investigated the adsorption of anionic surfactants in Berea sandstone at different conditions of temperature and salinity. They found that the adsorption of the anionic surfactants from a low salinity brine is low, but increases substantially at moderate salinities, and observed a trend of increasing adsorption with decreasing surfactant solubility.

Varadaraj et al.[41] used Wilhelmy plate measurements to study the dynamic contact angles of Guerbet sulfate (branched hydrophobic tail) and monodisperse ethoxy sulfate surfactants (linear hydrophobic tail) on the Teflon-water-air interface. Comparison of C16 linear with C16 Guerbet surfactants revealed that hydrocarbon chain branching decreases both the advancing and receding contact angles by about 30^0, representing increased water-wetting effectiveness. This change was attributed to increased structural rigidity of the branched hydrophobic tail group as well as increased area of coverage.

Varadaraj et al.[42] also evaluated the influence of the composition and structure of the hydrophobic tail group on wettability alteration of hydrophobic sand packs using capillary penetration wetting techniques. The composition of the surfactant tail group and

its branching influenced wetting. The wetting rate (rate of imbibition at half saturation) is ranked as ethoxylates > sulfates > ethoxy sulfates. However, wetting effectiveness (maximum amount of water imbibed at equilibrium) was observed as sulfates > ethoxylates. Tail group branching increases the wetting rate and effectiveness.

Kwok et al.[43] studied the propagation and adsorption of an anionic surfactant in Berea sandstone cores and reported dramatic surfactant loss and slower propagation as sodium chloride concentration increased. Increasing the pH of the surfactant slug from 6 to 12 reduced the surfactant loss by nearly thirty percent at a given sodium chloride and surfactant concentration, surfactant loss decreases as the injection flow rate increases.

Thomas et al.[44] studied chemical methods for heavy oil recovery and found that an important process efficiency parameter in the enhancement of oil recovery by the use of surfactants is the surfactant consumption, in lb/bbl of oil produced. They reported that the surfactant consumption would be in the range of 7 to 35 lb/bbl using the expression,

Consumption = 0.035053 (ppm) (Slug PV) (%Recovery)(S_{or})

where ppm is the surfactant concentration in ppm, Slug PV is the volume injected measured in number of pore volumes, S_{or} is the oil saturation at slug injection, expressed as fraction and % Recovery is oil recovery as a % of this oil saturation. However, the use of surfactants to enhance oil recovery is limited by costs as the cost of suitable surfactants can vary from $0.50 to 2.00 per lb. The cost has been decreasing but it is linked to oil prices.

Chen et al.[4] performed dilute surfactant imbibition tests on vertically oriented dolomite cores of the Yates field and found that additional oil is produced when compared with normal brine imbibition. They reported that this additional oil recovery is

due to oil-water interfacial tension reduction and wettability alteration. They measured the U.S.B.M wettability indices and showed that dilute surfactants have shifted the wetting characteristics of the Yates rocks toward less oil-wet.

Spinler et al.[45] conducted spontaneous imbibition tests on North Sea reservoir chalk plugs that were moderately water-wet at ambient and reservoir temperatures using low concentrations of surfactants. They found that oil recovery improves with low concentrations of surfactant for spontaneous and forced imbibition of water. They attributed this improvement to wettability alteration rather than reduction in interfacial tension. They also found that surfactant adsorption can be reduced if the surfactant concentration is kept below critical micelle concentration.

Kuhlman et al.[46] studied the adsorption and propagation of surfactants in Berea cores and found that surfactant adsorption in sandstones is reduced when the surfactant concentrations are kept below their CMCs. They reported that the adsorption can be minimized by reducing the ethoxylate chain length in alcohol ethoxy sulfonates and by blending un ethoxylated with ethoxylated sulfonates.

Najurieta et al.[47] studied spontaneous imbibition and forced displacement mechanisms in water-wet rocks with and without surfactants at different temperatures and found that spontaneous imbibition is an important production mechanism in water-wet rocks and that surfactants and high temperature accelerate the imbibition mechanism.

Wang et al.[48] introduced a new type of surfactant by synthesizing the anionic and nonionic surfactants for field use. This surfactant can reduce the interfacial tension to super low values even in high salinity formations.

Berger et al.[49] synthesized anionic surfactants by simultaneously alkylating and sulfonating aromatics. This new family of anionic surfactants can be used at low concentration levels to produce ultra-low interfacial tensions, have high salt tolerance and emulsions and corrosion can be minimized.

2.4 Measurement of Relative Permeability

Relative permeability describes the ability of the porous system to conduct one fluid when two or more fluids are present. Relative permeabilities are used to predict the oil-water flow characteristics in reservoirs.

The relative permeability of a rock to each fluid phase can be measured in a core sample by steady-state or unsteady-state methods. In a steady-state method, a fixed ratio of fluids is forced through the test sample until saturation and pressure equilibrium are established. The mathematical analysis of the unsteady-state procedure is more difficult. The theory developed by Buckley and Leverett[50] and extended by Welge[51] is used for the measurement of relative permeability under unsteady-state conditions.

2.4.1 Steady-State Methods[52]

2.4.1.1 Penn-State Method

This method was designed by Morse et al.[53] and later modified by Osoba et al.[54], Henderson and Yuster[55], Caudle et al.[56] and Geffen et al.[57] The sample is mounted between two rock samples which are similar to the test sample. This arrangement reduces the end effects due to capillary forces and also promotes mixing of the fluids before they enter the sample. Then, the sample is saturated with one fluid phase and the flow rate of this phase is adjusted until a predetermined pressure gradient is obtained. The second phase is injected at a low rate and flow of the first phase is slightly reduced so that the

pressure differential across the system remains constant. After an equilibrium condition is reached, the two flow rates are recorded and the percentage saturation of each phase within the test sample is determined by removing the test sample from the assembly and weighing it.

After fluid saturations are determined, the apparatus is assembled again to establish a new equilibrium condition at a higher flow rate for the second phase and the fluid saturations are redetermined. This procedure is repeated at higher saturations of the second phase until the complete relative permeability curve has been established.

2.4.1.2 Single-Sample Dynamic Method

This method was developed by Richardson et al.,[58] Josendal et al.,[59] and Loomis and Crowell[60]. The apparatus and the experimental procedure differ from the Penn-State method primarily in the handling of end effects. In this method, the two fluids are injected simultaneously through a single core. The end effects are minimized by using relatively high flow rates so that the region of high wetting phase saturation at the outlet face of the core is small. The saturation gradients are determined by using expressions developed from Darcy's law.

2.4.1.3 Stationary Fluid Method

Leas et al.[61] developed this technique for measuring permeability to gas with the liquid phase held stationary within the core by capillary forces. The flow rates must be small so that the liquid is not displaced during the test. This technique was modified by Osoba et al.,[54] who held the liquid phase stationary within the core with barriers which were permeable to gas but not to the liquid. Osoba et al.[54] observed that relative

permeability to gas determined by the stationary liquid method was in good agreement with values measured by other techniques.

2.4.1.4 Hassler Method

This technique was developed by Hassler[62] and was later modified by Gates and Lietz[63], Brownscombe et al.,[64] and Josendal et al.[59] Semi permeable membranes are installed at each end of the Hassler test assembly. These membranes keep the two fluid phases separated at the inlet and outlet of the core, but allow both phases to flow simultaneously through the core. The pressure in each fluid phase is measured separately through a semi permeable barrier. By adjusting the flow rate of the non- wetting phase, the pressure gradients in the two phases can be made equal, equalizing the capillary pressures at the inlet and outlet of the core. This procedure provides a uniform saturation throughout the length of the core (even at low flow rates), and thus eliminates the capillary end effect.

2.4.1.5 Hafford Method

This method was developed by Richardson et al.[58] In this method, the non-wetting phase is injected directly into the sample and the wetting phase is injected through a disc which is impermeable to the non-wetting phase. The central portion of the semi permeable disc is isolated from the remainder of the disc by a small metal sleeve. This central portion of the disc is used to measure the pressure in the wetting fluid at the inlet of the sample. The nonwetting fluid is injected directly into the sample and its pressure is measured through a standard pressure tap machined into the Luicite surrounding the sample. The pressure difference between the wetting and the non-wetting fluid is a measure of the capillary pressure in the sample at the inflow end.

2.4.1.6 Dispersed Feed Method

This technique was developed by Richardson et al.[58] In this method, the wetting fluid enters the test sample by first passing through a dispersing section, which is made of a porous material similar to the test sample. The dispersing section distributes the wetting fluid so that it enters the test sample more or less uniformly over the inlet face. The non-wetting phase is introduced into radial grooves which are machined into the outlet face of the dispersing section, the junction between the dispersing material and the test sample.

2.4.2 Unsteady-State Method[52]

Unsteady-state relative permeability measurements can be made more rapidly than steady-state measurements. Hence, unsteady-state measurements are employed for most laboratory measurements of relative permeability.

Unsteady-state displacement is characterized by the injection of one fluid into a core that contains a low or connate saturation of that fluid and which is intended to displace the mobile portions of a second fluid.

During two-phase flow, the flow rate of each phase is related to a pressure drop gradient by means of Darcy's law,

$$q_i = \frac{A.K_{ei}.\Delta p_h}{L\mu} \qquad \text{----------} \quad (2a)$$

and

$$K_{ei} = K.K_{ri} \qquad \text{----------} \quad (2b)$$

where subscript i denotes either wetting or non-wetting phase. The effective permeabilities (K_{ei}) to each phase depend on the saturation and saturation history of the phases. During single-phase flow when only one phase is present, the effective permeability to that phase is a maximum and equal to absolute permeability.

At any point when two phases flow simultaneously, a difference in the pressure between the phases (i.e., capillary pressure) usually exists. Capillary pressure depends on local curvatures of the fluid/fluid interfaces, which in turn depend on saturation, saturation history, wettability and pore geometry.

Laboratory unsteady-state displacement process can be affected by discontinuities at the inlet and more importantly the outlet of the core. When only one phase is entering or leaving the core, the capillary pressure and the effective permeability correspond to a maximum saturation of that phase. However, when the two phases are existing in the core simultaneously, the situation is different. At the core exit, the difference in the pressure between the phases will be extremely low. The only saturation at which this must be satisfied is in the vicinity of zero capillary pressure. The pressure drops within each phase near the exit must satisfy Eq.2. It is usually assumed that the exit boundary condition for simultaneous two-phase flow is zero capillary pressure.

In designing experiments to determine relative permeability by the unsteady-state method, it is necessary that:

1. The pressure gradient must be large enough to minimize capillary pressure effects.
2. The pressure differential across the core must be sufficiently small compared with the total operating pressure to minimize compressibility effects.
3. The core must be homogeneous.
4. The flow rate and the fluid properties must be held constant during the test.

The wettability measurement technique based on unsteady-state relative permeability developed by Rao e tal.[65] is used in the present study. A scaling criterion suggested by

Leas and Rapaport[66] has been used to remove the dependence of oil recovery on displacement rate and system length. This scaling causes the capillary pressure gradient in the direction of flow to be small compared with the imposed pressure gradient and is expressed as

$LV\mu \geq 1$ ---------- (3)

where L is the system length (in centimeters), μ is displacing phase viscosity (in centipoise) and V is velocity (in centimeters per minute). The criterion given in Eq.3 invariably is met within the reservoir because of the large distances between injector and producer. When using reservoir core samples less than about 30 cm long, Eq.3 normally is satisfied by using injection rates that are much higher than those which occur in the reservoir. Therefore, the preferable way of conducting a displacement test, both for determining relative permeability and for assessing enhanced recovery potential is to use the unsteady-state approach described above and then simulate the core displacements to history match the relative permeabilities.

2.5 Wettability Measurements

Wettability is usually defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid. The contact angle subtended by the oil-water interface against the rock surface is the universal measure of wettability. More specifically, wettability is characterized by the water-advancing contact angle since it corresponds to oil production scenario in the reservoir.

The quantitative methods of characterizing wettability of a porous medium are contact angle measurements, the Amott test and the USBM test. The qualitative methods are imbibition, microscope examination, flotation, glass slide, relative permeability

curves, capillarimetric method, displacement capillary pressure, permeability/saturation relation ships and the reservoir logs. Anderson[67] provides brief description of all these methods along with pertinent references.

Although, no single accepted method exists for accurate characterization of wettability, the three quantitative methods are most widely used for laboratory measurements.

2.5.1 Quantitative Methods[67]

2.5.1.1 Contact Angle Method

The contact angle is the best method for measuring wettability when pure fluids and artificial cores are used[68]. This method is also used to determine whether a crude oil can alter wettability and to examine the effects of temperature, pressure and brine chemistry on wettability. The methods that are generally used in the petroleum industry are sessile drop technique, modified form of sessile drop technique, Wilhelmy Plate technique and the Dual-Drop Dual-Crystal (DDDC) technique.

Relationship between wettability and contact angle:

When the contact angle is between 0 and 60 to 75^0, the surface is preferentially water – wet and when it is between 180 and 105 to 120^0, the surface is preferentially oil wet. If the contact angle is between 60 to 75^0 and 105 to 120^0, neither fluid preferentially wets the solid i.e., intermediate wettability.

The limitations of this method citied in the literature are:

1) The contact angle measured cannot take into account the surface roughness, heterogeneity and the complex geometry of the reservoir rock.

2) No information can be gained about the presence or absence of permanently attached organic coatings on reservoir rocks.
3) It is difficult to get exact and reproducible contact angle measurements.

Due to all these reasons, the wettability characterization by the contact angle measurements does not appear to be preferred by the petroleum industry. However, it is important to note that the DDDC technique has generated the exact, consistent and reproducible values of contact angles for several reservoir samples[69]. Recently, Vijapurapu and Rao[27] measured the effect of surface roughness on contact angles using this technique. Therefore, it appears that most of the past concerns about contact angles are being addressed by the DDDC technique. Hence, we prefer to use the DDDC technique for measuring the contact angles as this method has proven to be sensitive and reliable yielding reproducible results.

2.5.1.2 Amott Method

The Amott test for characterizing wettability is based on natural imbibition and forced displacement of oil and water from the cores. Since, the oil recovery from a fractured reservoir like Yates occurs mainly due to spontaneous imbibition of water, this method is of major interest and thoroughly discussed in the following sections.

The main principle of this method is that the wetting fluid will generally imbibe spontaneously into the core, displacing the non-wetting one. The ratio of spontaneous to forced imbibition is then used to reduce the influence of other factors such as relative permeability, viscosity and the initial saturation of the core. The test measures the average wettability of the core using the procedure that involves five stages.

1) The test begins at residual oil saturation to waterflood, so, the fluids are reduced to S_{or} by forced displacement of brine.
2) The core is immersed in oil for 20 hours and the amount of water displaced by spontaneous imbibition of oil, if any, is recorded as V_{wsp}.
3) The water is displaced to the initial water saturation with oil, and the total amount of water displaced (by imbibition and by forced displacement of oil) is recorded as V_{wt}.
4) The core is immersed in brine for 20 hours, and the volume of oil displaced, if any, by spontaneous imbibition of water is recorded as V_{osp}.
5) The oil remaining in the core is displaced by water to S_{or} and the total amount of oil displaced (by imbibition and by forced displacement of water) is recorded as V_{ot}.

The forced displacements of oil to S_{or}, and water to S_{wi} may be conducted using a centrifuge or by mounting the core in a coreflood apparatus and pumping the displacing fluids into the core.

The test results are then expressed as follows:

1) The displacement by oil ratio: the ratio of water volume displaced by spontaneous oil imbibition alone, V_{wsp} to the total displaced by oil imbibition and centrifugal (forced) displacement V_{wt},

$$\delta_o = V_{wsp} / V_{wt} \quad \text{----------} \quad (4)$$

2) The displacement by water ratio: the ratio of the oil volume displaced by spontaneous water imbibition alone, V_{osp}, to the total oil volume displaced by imbibition and centrifugal (forced) displacement V_{ot},

$$\delta_w = V_{osp} / V_{ot} \quad \text{---------- (5)}$$

Preferentially water-wet cores are characterized by a positive displacement by water ratio (δw) and a zero value for the displacement by oil ratio (δ_o). The displacement by water ratio approaches unity as the water wetness increases. Similarly, oil wet cores have a positive displacement by oil ratio (δ_o) and a zero displacement by water ratio (δ_w). Both the ratios are zero for neutrally wet cores indicating the absence of spontaneous imbibition of either oil or water.

The 20 hour arbitrary time limit for the two periods of imbibition were probably chosen to allow completion of the test in a reasonable length of time. Completion of imbibition, however, can some times take several weeks, and when the system is near neutral wettability, spontaneous imbibition is quite low and slow. If the imbibition is not allowed to go to completion, the values of δ_o and δ_w will be underestimated, leading to erroneous conclusions regarding the wettability of core samples. Therefore, rather than setting a 20-hour time limit on the spontaneous imbibition periods, the amount of fluid displaced should be measured periodically and examined graphically until a stable equilibrium value is attained.

A number of researchers used a modification of the Amott wettability test called the "Amott-Harvey relative displacement index". This procedure has an additional step in the core preparation before the test is run: the core is centrifuged first under brine and then under crude oil to reduce the plug to initial water saturation (IWS). The displacement by water and displacement by oil ratios are then calculated by the Amott method. The Amott – Harvey relative displacement index is the displacement by water ratio minus the displacement by oil ratio.

$$I = \delta_w - \delta_o = (V_{osp} / V_{ot}) - (V_{wsp} / V_{wt}) \quad \text{----------} \quad (6)$$

This combines the two ratios into a single wettability index that varies from +1 for complete water wetness to –1 for complete oil wetness with zero representing the neutral wettability. Cuiec[70] states that the system is water-wet when $+0.3 \leq I \leq 1$, intermediate wet when $-0.3 < I < 0.3$ and oil wet when $-1 \leq I \leq -0.3$.

The Amott test measures the total volume of spontaneous and forced imbibition of oil and water. If we are able to measure the imbibition rates during the spontaneous imbibition measurements, then the wettability of the core can be determined from both the Amott wettability index and the spontaneous imbibition rates. This offers some advantages over the standard Amott test because it is based on additional data.

The main problem with the Amott wettability test is that they are insensitive near neutral wettability. Further more, Amott test does not discriminate adequately between the systems that give high values of wettability index to water and are collectively described as very strongly water - wet.

2.5.1.3 USBM Wettability Index

This test also measures the average wettability of the core. It is relatively rapid, requiring a few days to test four to eight plugs. This measures wettability by measuring the area under the curve obtained by plotting the capillary pressure against the water saturation. This method uses the ratio of areas under the two capillary pressure curves to calculate the wettability index, W, defined by the Eq. 9 to characterize the wettability of the core.

$$W = \log (A_1/A_2) \quad \text{----------} \quad (7)$$

where A_1 and A_2 are the areas under the oil and brine drive curves respectively. When W is greater than zero, the core is water-wet, and when W is less than zero, the core is oil-wet. A wettability index near zero means the core is neutrally wet. The larger the absolute value of W, the greater the wetting preference.

A major advantage it has over the Amott wettability test is its sensitivity near neutral wettability. The disadvantage of this method is that the USBM wettability index can only be measured on plug – size samples because the samples must be spun in a centrifuge.

2.5.2 Qualitative Methods[67]

2.5.2.1 Imbibition Method

This method is the most commonly used as it gives a quick and rough idea of the wettability without requiring any complicated equipment.

In an imbibition test, a core at initial water saturation is first immersed in brine underneath a graduated cylinder and the rate and amount of oil displaced by brine imbibition are measured. The core is strongly water-wet if large volumes of brine are rapidly imbibed, while lower rates and smaller volumes imply a more weakly water-wet core. If no water is imbibed, the core is either oil wet or neutrally wet. Non water-wet cores are then driven to residual oil saturation and submerged in oil. The imbibition apparatus is inverted, with the graduated cylinder below the core to measure the rate and volume of water displaced by oil imbibition. If the core imbibes the oil, it is oil-wet. The strength of oil-wetness is indicated by the rate and volume of oil imbibition. If neither oil nor water is imbibed, the core is neutrally wet. Some cores will imbibe both oil and water. These cores have either fractional or mixed wettability.

2.5.2.2 Microscope Examination

In this method, the wettability is determined from a description of the flow on a single pore level in an idealized porous medium during waterflooding. This description includes the structure of the residual oil and the changes in the location of the oil and water that occur during waterflooding. If the system is strongly water-wet, the water surrounds the grains as a thin film. The large pools of residual oil rest on a water film, while the smaller drops of residual oil form spherical drops in the center of the pores. If the system is intermediately wet, both oil and water will be found in contact with the rock surfaces and both can be found in the small pores. Finally, if the system is oil-wet, the roles of the oil and water are reversed. The oil forms a film around the grain surfaces and is found in the small pores, while the water rests on an oil film or forms small spheres.

2.5.2.3 Floatation Methods

This method is fast and preferable only for strongly wetted systems. In this method, water, oil and sand are placed in a glass bottle. The bottle is shaken and the fate of sand grains is observed. If the system is strongly water-wet, clean sand grains will settle to the bottom of the bottle. Sand grains placed in oil will aggregate and form small clumps of grains surrounded by a thin layer of water. If the system is oil wet, some of the grains can be suspended at the oil/water interface. Oil-wet sand grains in the water will clump together, forming small oil globules coated with sand.

2.5.2.4 Glass Slide Method

This method assumes that a glass surface is representative of the reservoir rock. In this method, a clean, dry glass microscope slide is suspended in a layer of crude oil floating on water in a transparent container and aged. The glass slide is then lowered into

the water. If the slide is water-wet, the water quickly displaces the oil on the slide. On the other hand, if the slide is oil-wet, a stable oil-wet film is formed and the oil is very slowly displaced.

2.5.2.5 Relative Permeability Method

Wettability affects relative permeability because it is a major factor in the control of the location, flow and spatial distribution of fluids in the core. So, this method is used in the present study to discern wettability alterations induced by the surfactants through relative permeability modifications.

In this method, Craig's rules of thumb[71] are used to distinguish between strongly water-wet and oil-wet systems based on relative permeability curves.

1) Connate water saturations are usually greater than 20 to 25% PV in a water-wet rock, but less than 10% PV in an oil-wet rock.
2) Water saturation at which oil and water relative permeabilities are equal is generally greater than 50% in water-wet rocks and less than 50% for oil-wet ones.
3) The relative permeability to water at flood out is generally less than 30% in water-wet rocks, but from 50 to 100% in oil-wet ones.

These relative permeabilities are based on the oil permeability at the connate water saturation.

2.5.2.5.1 Imbibition

Imbibition, the displacement process in which wetting phase saturation increases corresponds to the displacement of a non-wetting phase by a wetting phase. The recovery of oil during water injection in a water-wet rock is an example for imbibition. At the start

of imbibition process, the core is assumed to be uniformly saturated with non-wetting fluid at the initial wetting phase saturation corresponding to a connate condition.

2.5.2.5.2 Drainage

Drainage, the displacement of a wetting phase by a non-wetting phase, corresponds to the recovery of oil during water injection in an oil -wet rock. An oil bank, built up as a result of tertiary recovery in a water-wet oil reservoir, would exhibit drainage characteristics at its leading edge and the imbibition behavior at the trailing edge. The displacement of water by oil in a water-wet rock, such as commonly occurs in core tests during the establishment of initial saturation conditions before conducting a water-flood, is another prime example of a drainage process.

2.5.2.5.3 Hysteresis

In many strongly wetted systems, the wetting-phase relative permeability is primarily a function of its own saturation. In other words, the hysteresis between the wetting-phase drainage and imbibition relative permeabilities is much smaller than the non-wetting phase hysteresis. In addition, wetting-phase relative permeabilities are very similar for both two and three phase relative permeability measurements in strongly wetted systems at a given wetting-phase saturation.

2.5.2.6 Permeability/Saturation Relationships

In this method, the wettability is characterized based on connate water saturation and air permeability. A qualitative measure of wettability is obtained by plotting the connate water saturation vs. air permeability. If the core is oil-wet, the average connate water saturation is relatively low and the plot is nearly vertical extending over only a

small saturation interval. For the water-wet case, the curve has a gentle slope and extends over a large saturation interval.

2.5.2.7 Capillary Pressure Curves

In this method, the areas under the capillary pressure curves are used to measure the wettability of the core. This is the basis of the quantitative USBM method discussed earlier.

2.5.2.8 Capillarimetric Method

In this method, the adhesion tension $\sigma\cos\theta$ which is also called as displacement energy is used to characterize the wettability of the core.

If the core is water-wet, the displacement energy is positive and the displacement energy is negative if the core is oil-wet.

2.5.2.9 Displacement Capillary Pressure

In this method, the wettability is characterized based on apparent contact angles calculated by using the displacement or threshold capillary pressure.

2.5.2.10 Reservoir Logs

There are two methods available to measure the wettability of reservoir rock with logs. The first method is based on the fact that the electrical resistivity of an oil-wet rock is higher than that of a water-wet rock at the same saturation. The formation is first injected with brine and then resistivity logs are run. Next, the formation is injected with the same brine having reverse wetting agent to change a water-wet formation to oil-wet one. The logs are rerun to determine the reservoir wettability by comparing the two measurements.

The second method involves comparison of logs with core data. The saturation of the formation measured with logs is converted into a capillary pressure curve and then by comparing this curve with a capillary pressure curve of a clean water-wet core, the wettability can be characterized.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Reagents

Analytic grade reagents were used in the experiments. Decane and the salts that were used for synthetic brine preparation were from Fisher Scientific having a purity of 99.9%. Deionized water was from the Water Quality Laboratory at Louisiana State University. The Berea sandstone used in the experiments was from Cleveland Quarries, Ohio. Yates crude oil, nonionic surfactant (ethoxy alcohol) and anionic surfactant (ethoxy sulphate) were supplied by Marathon Oil Company. The crude oil was kept under nitrogen blanket to prevent oxidation and filtration of the brine was done using Sterivac^{TM} filter units.

3.2 Experimental Setup

A coreflood apparatus was built for measuring relative permeabilities (Figure 1). It consisted of (1) a pump for injecting different fluids into the core (2) a pressure gauge to measure the pressure drop across the core during the floods (3) core holder inside which the core is placed and (4) a measuring cylinder to measure the flow rates at the outlet. The dead volumes of all the flow lines were measured and accounted for in all the material balance calculations

3.3 Experimental Procedure

Synthetic brine matching the Yates reservoir brine composition is used in all core floods. The coreflood apparatus is used to estimate oil recovery, saturations of oil and water and the end-point effective permeabilities. A coreflood simulator uses these data to

estimate oil/water relative permeabilities. The series of experiments conducted in this study are shown in Table 1.

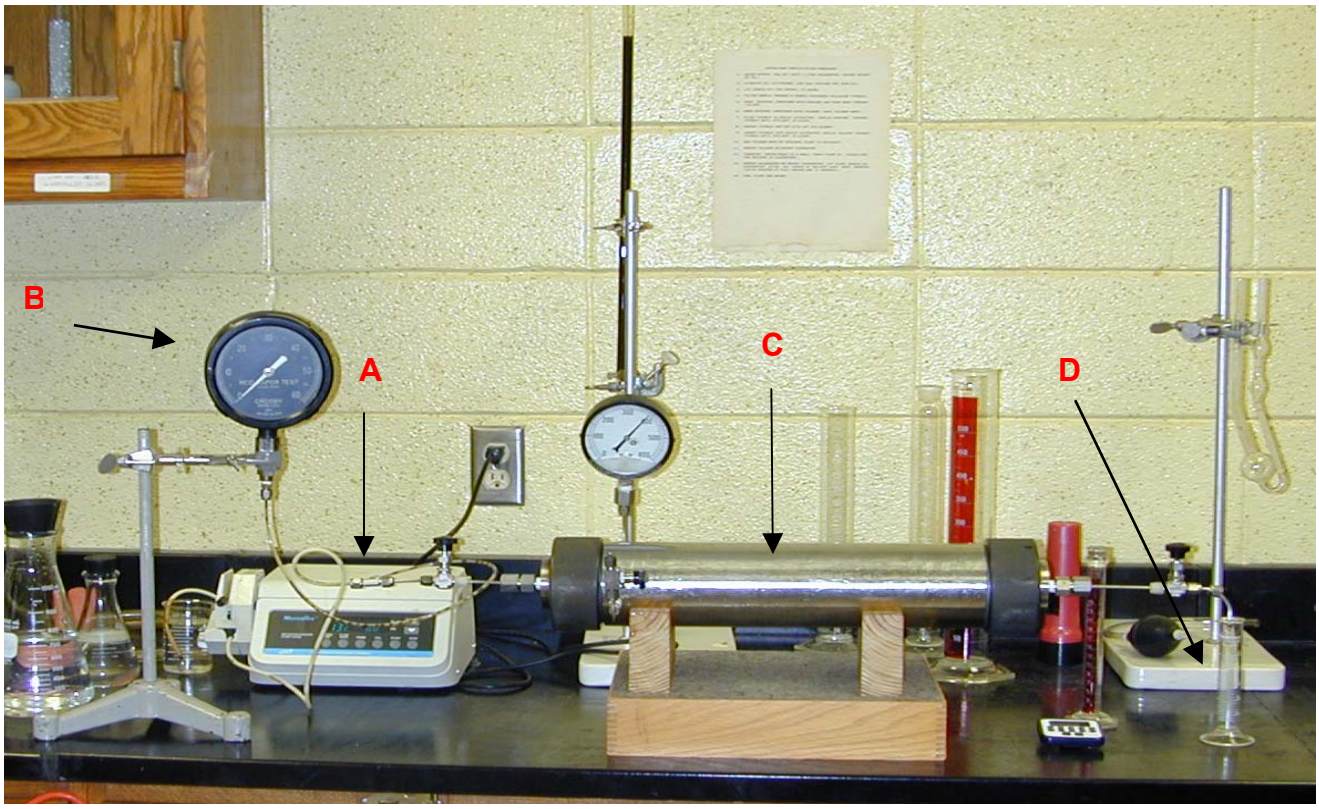


Figure 2: Coreflood Apparatus (A: Pump; B: Pressure gauge; C: Core holder; D: Measuring cylinder).

Table 1: List of Experiments Conducted and Properties of Cores Used in this Study

Set	System	Surfactant	Oil	Core Properties			
				L (cm)	D (cm)	K (md)	ϕ (%)
1	Non-reactive	Nonionic	Decane	7.553	3.720	402	22.06
2	Reactive	Nonionic	Yates	8.615	3.705	400	22.06
3	Non-reactive	Anionic	Decane	15.60	5.054	465	21.31
4	Reactive	Anionic	Yates	15.50	5.054	465	21.11

All the four sets of experiments used Yates synthetic brine and Berea sandstone. In each set, five surfactant concentrations were used (0, 500, 1500, 3500 and 5000 ppm), thus bringing the total number of floods to 20.

First two sets of experiments were conducted on a shorter Berea core. A larger core was used in the latter two sets in order to increase the pore volume. The surfactant concentrations of 500 ppm, 1500 ppm, 3500 ppm and 5000 ppm were chosen to resemble the field operations. Leas and Rapaport criterion[66] ($LV\mu = 1.0$) was used to calculate the stable volumetric flow rates to be used in each of the experiments to ensure all the floods are in a flow regime where the recovery is independent of injection flow rate.

The core was saturated with brine to determine its porosity and the absolute permeability. Then oil was injected at a flow rate of 2.0 cc/min for 2 pore volumes and 6.0 cc/min for 5 pore volumes to bring the core to initial water saturation (S_{wi}). Then a water flood was conducted using synthetic brine. The core was then brought back to S_{wi} by flooding with oil (n-decane/Yates crude oil). Then the effect of surfactant concentration on oil recovery was studied by carrying out several floods with synthetic brine containing different concentrations (500,1500,3500 and 5000 ppm) of each of the two surfactants (ethoxy alcohol and ethoxy sulphate). During each flood, pressure drop and oil and brine production were continuously monitored. A coreflood simulator was used to calculate oil-water relative permeabilities by history matching the pressure drop and the recovery data for each of the of the above core floods. These relative permeability data have been used to discern the wettability alterations induced by the surfactant solutions of varying concentrations.

3.4 Simulation of Corefloods to Determine Oil-Water Relative Permeabilities

The main purpose of these coreflooding experiments is to quantify and determine the relative permeabilities which are needed for reservoir simulation studies. Therefore, we have used a semi-analytical relative permeability model developed by Okazawa[72] to simulate the coreflooding experiments. This model was developed to suit the cases where the capillary pressure data was unavailable. Fractional flow theory is used to calculate the recovery and pressure drop at a given time after the start of the displacement. The pressure drop is computed by deriving the saturation profile in the core and thereby calculating the total mobility along the length of the core.

This model estimates relative permeabilities by minimizing the sum-of-squares of the weighted deviations of the experimental pressure and production histories from the calculated values. The relative permeabilities are generated using the following functions.

$$k_{ro} = (1 - S)^{e_o} . k_{rom} \quad \text{----------} \quad (8)$$

$$k_{rw} = S^{e_w} . k_{rwm} \quad \text{----------} \quad (9)$$

$$S = (S_w - S_{wi}) / (S_{wm} - S_{wi}) \quad \text{----------} \quad (10)$$

where S_w is the brine saturation, S_{wi} is the irreducible brine saturation, S_{wm} is the maximum brine saturation or $(1-S_{or})$, k_{ro} is the relative permeability to oil, k_{rw} is the relative permeability to brine, k_{rom} is the relative permeability to oil at S_{wi}, k_{rwm} is the relative permeability to brine at S_{or} and e_O and e_w are the Corey exponents.

CHAPTER 4

RESULTS AND DISCUSSION

Two main mechanisms behind the use of surfactants for enhancing oil recovery are reduction in interfacial tension and alteration of wettability. To discern the relative contribution from these two mechanisms, coreflood experiments were carried out in two different rock-fluids systems – one using Berea rock + Yates synthetic brine + decane which had no wettability effects (referred to as non-reactive system here onwards) and the other using Berea rock + Yates synthetic brine + Yates crude oil with its accompanying wettability effects (referred to as reactive system). Two types of surfactants were used, one nonionic (ethoxy alcohol) and the other anionic (ethoxy sulphate). The complete break up of experiments conducted in this study is shown in Table 1 of chapter 3. Characteristics of relative permeability curves including the initial water saturation, the end-point water relative permeability, the end-point oil relative permeability and the water saturation at cross-over point were used to infer wettability alterations induced by the surfactants. The rules-of-thumb used in this study to characterize wettability are summarized in Table 2.

Table 2: Rules-of-thumb used in this Study for Wettability Interpretation

S.No	Criterion	Water-Wet	Oil-Wet	Reference
1	Initial Water Saturation, S_{wi}	> 0.25	< 0.15	Craig[71]
2	Water Saturation at Cross-over Point	> 0.5	< 0.5	Craig[71]
3	End-point Relative Permeability to Water at S_{or}	< 0.3	> 0.5	Craig[71]
4	End-point Relative Permeability to Oil at S_{wi}	> 0.95	< 0.7 - 0.8	Thomas[73] Archer[74]

4.1. Nonionic Surfactant (Ethoxy Alcohol)

4.1.1. Non-Reactive System (Berea Rock + Yates Synthetic Brine + Decane):

Oil/water emulsion was formed during the coreflood experiments in this system strongly affecting relative permeability curves. This emulsion did not break down even for aging times of over 24 hours. These emulsions formed at all surfactant concentrations blocked the flow or caused very high pressure drops. The high pressure drops during primary drainage caused low end-point oil permeabilities which raises concerns about the rules-of-thumb (Table 2).

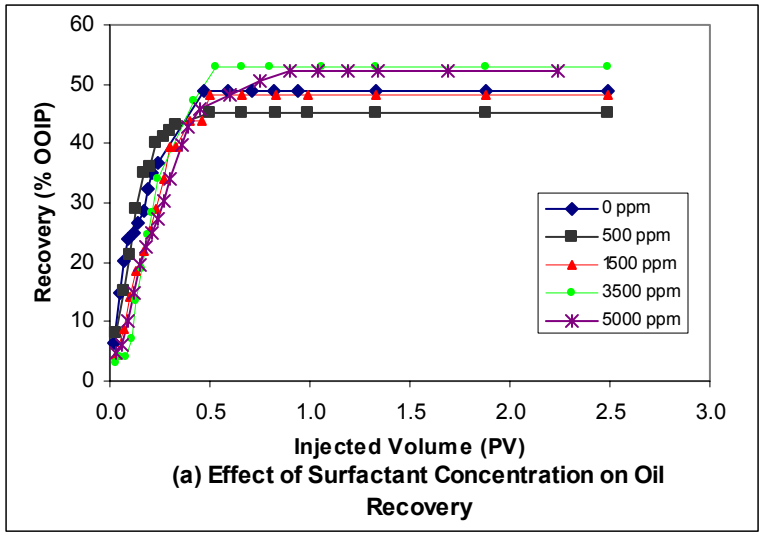
Relative permeabilities were estimated for the decane-Berea system at various nonionic surfactant concentrations (Table 3, Figures A1-A5 of Appendix). Only minor adjustments are done in end-point oil relative permeabilities to obtain acceptable history match of recovery and pressure drop. Figure 3 presents the effect of nonionic surfactant concentration on oil recovery, pressure drop, relative permeability ratio and fractional water flow.

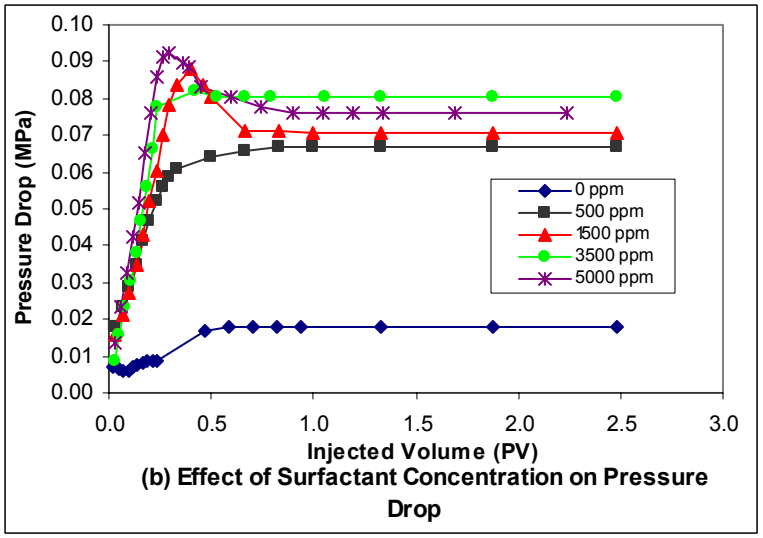
Relative permeability curves at 0 ppm surfactant concentration (Figure A1(c)) indicate water-wet characteristics (S_{wi} = 39% > 25%, $S_{w,c\text{-}o}$ = 55% > 50%, K_{rw} = 7.5% < 30%). The end-point oil relative permeability of 70% at S_{wi} is caused by emulsion formation.

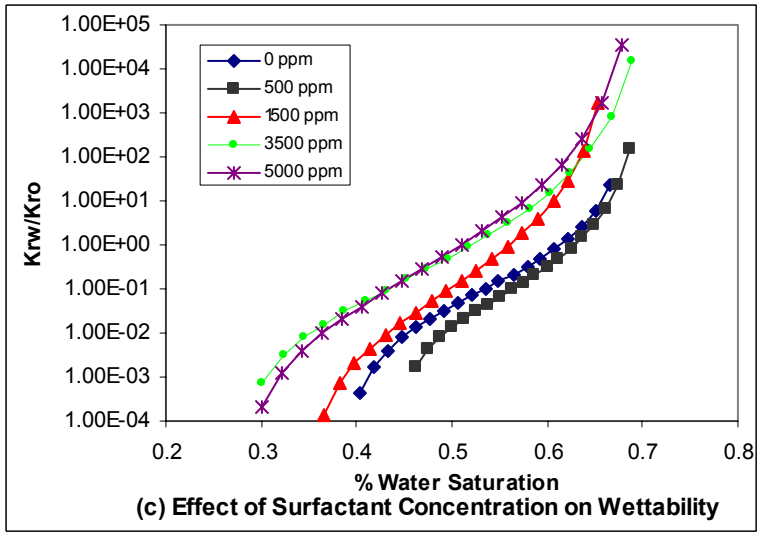
Relative permeability curves at 500 ppm surfactant concentration (Figure A2(c)) indicate water-wet / intermediate-wet characteristics (S_{wi} = 45% > 25%, $S_{w,c\text{-}o}$ = 56% > 50%, K_{rw} = 2.6% < 30%). The end-point oil relative permeability of 56% at S_{wi} is once again attributed to emulsion formation. Similar trends are observed in the characteristics of relative permeability curves at all other surfactant concentrations.

Table 3: Comparison between the Experimental and Simulator Results for waterflood of Decane in Berea Core at Various Nonionic Surfactant Concentrations

Case	Experimental					Simulator			
	Recovery (%OOIP)	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**
Brine	48	0.400	0.320	0.700	0.0840	0.390	0.320	0.700	0.0750
500 ppm	45	0.450	0.332	0.554	0.0905	0.450	0.300	0.554	0.0262
1500 ppm	47	0.365	0.362	0.425	0.0951	0.350	0.330	0.425	0.0255
3500 ppm	54	0.300	0.365	0.225	0.0900	0.280	0.290	0.225	0.0225
5000 ppm	54	0.285	0.375	0.208	0.0650	0.280	0.300	0.208	0.0275







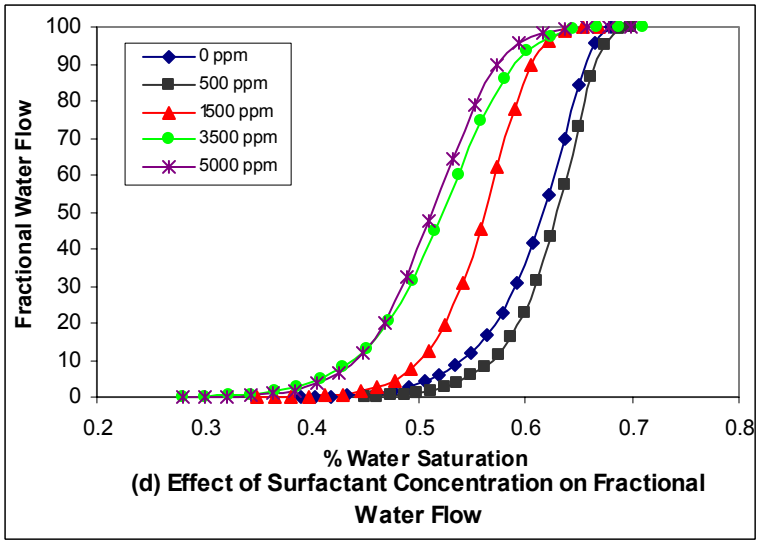


Figure 3: Coreflood Simulator Results for Waterflood of Decane in Berea Rock at Various Nonionic Surfactant Concentrations.

The salient observations made from the experimental results obtained for this non-reactive system are summarized below.

1) The oil recovery gradually increases from 45% to 54% as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm. These enhanced oil recoveries are attributed to the reduction in oil-water interfacial tension and not to wettability alteration as discussed below.
2) There is a significant change in the initial water saturation and it gradually decreases from 40% to 28% in these floods as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm, except for the case of 500 ppm surfactant concentration, where the initial water saturation is 45%. Thus, the initial water saturation is always greater than 25% for all these floods, indicating water-wet characteristics according to the Craig's rules.
3) The end-point relative permeability to water at residual oil saturation gradually decreases from 7.5% to 2.75% in these floods as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm and is always less than 30% of the end-point oil relative permeability for all these floods. These results also suggest water-wet characteristics.
4) There is a significant shift to the left in the water saturation at crossover-point from 55% to 45% in these floods as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm. This shift appears to indicate a shift from water-wet to less water-wet or intermediate-wet condition as the surfactant concentration is increased. However, emulsion formation is the reason for this shift and not wettability change.

5) There is a significant drop in the end-point relative permeability to oil at initial water saturation from 70% to 21% in these floods as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm. This significant drop in the end-point oil permeabilities appears to indicate a shift from water-wet / intermediate-wet to oil-wet nature as the surfactant concentration is increased. This shift is attributed mainly to high pressure-drops caused by the oil/water emulsion formations at higher nonionic surfactant concentrations and not wettability alteration.
6) The relative permeability ratio curves are gradually shifting to the left as the non-ionic surfactant concentration is increased. This shift appears to indicate a shift from water-wet to less water-wet or intermediate-wet condition. However, this shift is attributed to the formation of oil/water emulsion observed at all surfactant concentrations as noted earlier and not to wettability alteration.

From all the above considerations, it can be concluded that, the Berea rock + Yates synthetic brine + decane system is non-reactive as originally assumed and insensitive to wettability alterations in the presence of the nonionic surfactant. For further verification, experimentation is suggested to measure contact angles on Berea rock + Yates synthetic brine + decane system at various nonionic surfactant concentrations, using the DDDC technique.

From the plot of recovery against injected volume of Figure 3(a), it is observed that the recovery gradually increases as the surfactant concentration is increased from 0 ppm to 5000 ppm. However, there is a significant increase in the recovery (54%) at 3500 ppm surfactant concentration. Above 3500 ppm, the increase in recovery is small, suggesting

that 3500 ppm surfactant concentration is the optimum nonionic surfactant concentration for this system to maximize oil recovery.

The pressure drop gradually increases as the nonionic surfactant concentration is increased (Figure 3(b)). This unexpected phenomenon can be attributed mainly to the formation of oil/water emulsions observed during the core flooding experiments. At higher nonionic surfactant concentrations, the emulsions were much stronger, causing very high pressure drops and significant decline in end-point oil relative permeabilities.

4.1.2 Reactive System (Berea Rock + Yates Synthetic Brine + Yates Crude Oil):

Formation of oil/water emulsion was not observed during the coreflooding experiments in this system at different surfactant concentrations. Therefore, all the changes that were observed in the characteristics of relative permeability curves are due to wettability shifts.

The summary of experimental and simulator results for waterflood of Yates crude oil in Berea rock at various concentrations of the nonionic surfactant, ethoxy alcohol is shown in Table 4.

The history match of oil recovery, pressure drop and the resulting relative permeability curves obtained from the simulator for this system for different nonionic surfactant concentrations are shown in the Figures A6-A10 of Appendix. Figure 4 presents the effect of nonionic surfactant concentration on oil recovery, pressure drop, relative permeability ratio and fractional water flow.

The results from Table 4 indicate minor adjustments in end-point water relative permeabilities in the simulator to obtain acceptable history match of oil recovery and pressure drop at all nonionic surfactant concentrations used in this study.

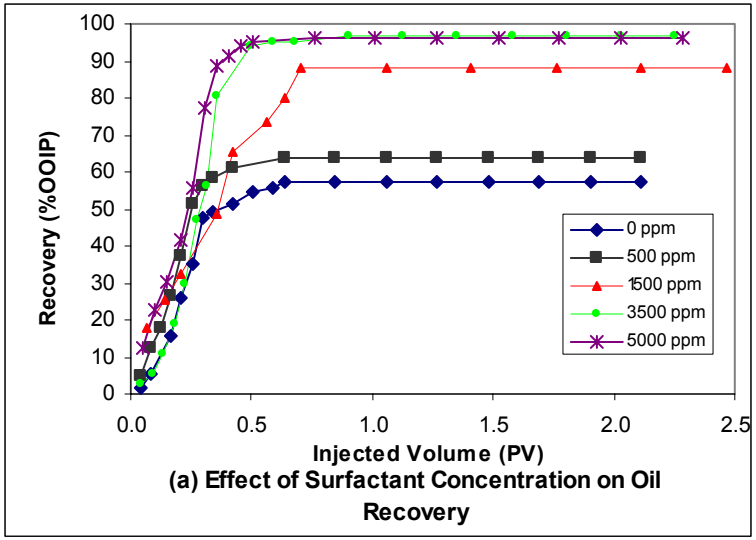
Relative permeability curves at 0 ppm surfactant concentration (Figure A6(c)) indicate water-wet characteristics (S_{wi} = 39% > 25%, $S_{w,c-o}$ = 60% > 50%, K_{rw} = 2.8% < 30% and k_{ro} = 0.97 > 0.95).

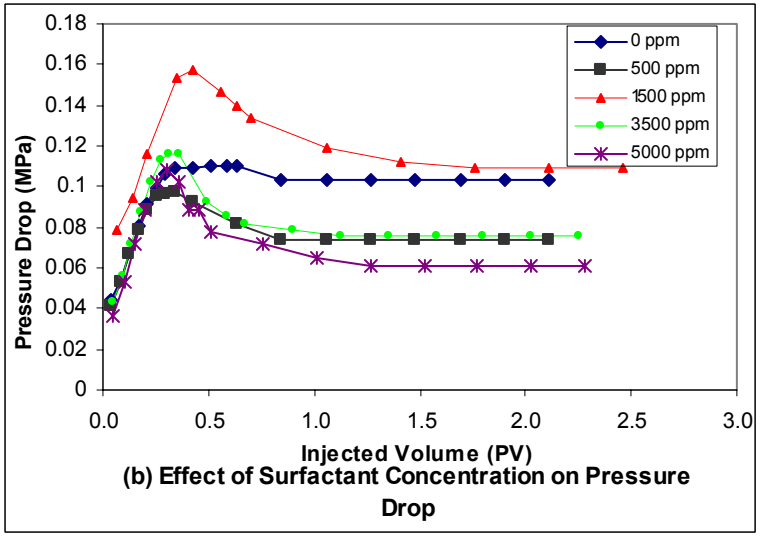
Relative permeability curves at 500 ppm surfactant concentration (Figure A7(c)) indicate strong water-wet characteristics (S_{wi} = 49% > 25%, $S_{w,c-o}$ = 70% > 50%, K_{rw} = 4.3% < 30%). However, the end-point oil relative permeability of 83% at S_{wi} indicates weakly water-wet or intermediate-wet nature.

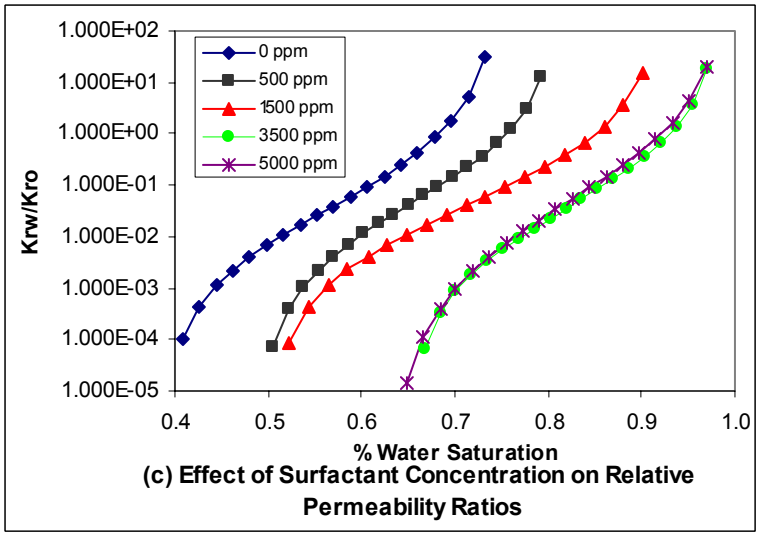
Similar trends are observed in the characteristics of relative permeability curves at higher nonionic surfactant concentrations.

Table 4: Comparison between the Experimental and Simulator Results for waterflood of Yates Crude Oil in Berea Core at Various Nonionic Surfactant Concentrations

Case	**Experimental**					**Simulator**			
	Recovery (%OOIP)	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**
Brine	56	0.400	0.290	0.970	0.0710	0.390	0.250	0.970	0.0280
500 ppm	62	0.500	0.210	0.830	0.1435	0.490	0.191	0.830	0.0430
1500 ppm	86	0.520	0.085	0.945	0.0950	0.500	0.077	0.945	0.0410
3500 ppm	94	0.650	0.038	1.000	0.1322	0.650	0.012	1.000	0.0350
5000 ppm	94	0.630	0.039	0.886	0.1483	0.630	0.013	0.886	0.0550







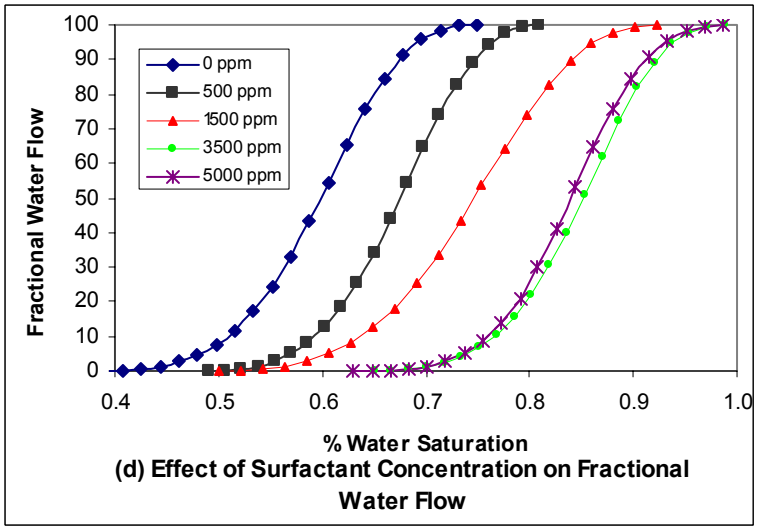


Figure 4: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Rock at Various Nonionic Surfactant Concentrations.

From the experimental results obtained from the water flood of Yates crude oil in Berea rock at various nonionic surfactant concentrations, the following observations are made.

1) Significant increase in oil recovery from 49% to 94% is observed as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm.
2) There is a significant change in the initial water saturation and it gradually varies from 40% to 65% in all these floods as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm. It is always greater than 30% for all these floods.
3) Significant change was not observed in the end-point relative permeability to water at residual oil saturation for all these floods. It remains almost the same and is always less than 30% of end-point oil relative permeability.
4) There is a significant shift to the right in the water saturation at crossover-point from 60% to 90% in these floods as the nonionic surfactant concentration is increased from 0 ppm to 5000 ppm.
5) There is a significant change (especially because of absence of emulsion) in the end-point relative permeability to oil at initial water saturation in these floods and it varies from 97% to 88% as the nonionic surfactant concentration increased from 0 ppm to 5000 ppm.
6) Relative permeability ratio curves are shifting to the right as the nonionic surfactant concentration is increased.

The very high oil recoveries observed in this system at higher surfactant concentrations indicate that the system is neither water-wet nor oil-wet. Therefore,

Craig's rules-of-thumb[71] are not applicable to infer wettability shifts for this system as these rules are used only to distinguish between strongly water-wet and oil-wet systems based on relative permeability curves. Hence, the ratios of water/oil relative permeabilities are used to interpret the wettability states for this system. From the plot of relative permeability ratios against water saturation of Figure 4(c), it is observed that the curves are shifting to the right as the nonionic surfactant concentration is increased. This type of relative shifts in the relative permeability ratio curves indicate development of a mixed-wettability condition[65,75]. The very low residual oil saturations at higher nonionic surfactant concentrations (Table 4) also indicate the development of Salathiel[76] type mixed-wettability as the nonionic surfactant concentration is increased. This is further evidenced in the oil recovery plot of Figure 4(a) where recoveries are significantly higher at higher nonionic surfactant concentrations.

The system is initially strongly water-wet when nonionic surfactant was not present. Hence, the rock surface is covered with water and oil exists in the form of globules in the middle of the bigger pores. Thus there would be a film of water between the rock surface and oil globules. In the presence of a water-soluble nonionic surfactant, this thin water film could become unstable[77] due to the extent of adsorption of surfactant molecule at the rock-water interface relative to that at the oil-water interface and due to the orientation of surfactant molecules at these interfaces. This instability of the liquid film at the interface results in oil/water/rock interactions forming a continuous oil-wet path for favorable displacement of oil. This is nothing but the development of mixed-wettability, as envisioned by Salathiel[76].

From all these experimental results and the related explanations, the system is water-wet in the absence of nonionic surfactant and gradually shifts to mixed-wet as the nonionic surfactant concentration is increased. However, to substantiate the development of mixed-wettability condition due to the presence of nonionic surfactant, further experimentation should measure dynamic contact angles on Berea rock + Yates synthetic brine + Yates crude oil system at various nonionic surfactant concentrations, using the DDDC technique.

The recovery gradually increases as the nonionic surfactant concentration is increased (Figure 4 (a)). There is significant increase in the recovery (94%) at 3500 ppm nonionic surfactant concentration when compared to the recovery (56%) at 0 ppm nonionic surfactant concentration. Above 3500 ppm surfactant concentration, the increase in oil recovery is small suggesting that 3500 ppm surfactant concentration is the optimum concentration for this system to achieve maximum oil recovery. Furthermore, the recoveries at each nonionic surfactant concentration are much higher in the reactive system of Berea rock + Yates synthetic brine + Yates crude oil when compared to the recoveries at the same nonionic surfactant concentrations in the non-reactive system of Berea rock + Yates Synthetic brine + decane. This observation further substantiates that the Berea rock + Yates Synthetic brine + decane system is non-reactive and neutral to wettability alterations and the significant increase in oil recovery observed while using the Yates crude oil is mainly due to wettability alteration.

From the plot of pressure drop against injected volume of Figure 4(b), the pressure drop gradually decreases as the nonionic surfactant concentration is increased. This phenomenon is attributed to the absence of oil/water emulsions observed during the

coreflooding experiments in this reactive system of Berea rock + Yates synthetic brine + Yates crude oil with the nonionic surfactant.

4.2. Anionic Surfactant (Ethoxy Sulphate)

4.2.1. Non Reactive System (Berea rock + Yates Synthetic brine + Decane):

The formation of oil/water emulsion was observed during the corefloods in this non-reactive system also, which has a strong impact on relative permeability curves. Therefore, the wettability shifts inferred from the characteristics of relative permeability curves are considered to be doubtful for this system. These emulsions at surfactant concentrations of 500 ppm and above caused serious difficulties in the coreflooding experiments resulting in no-flow situations or very high pressure drops, as in the case considered in section 4.1.1.

The summary of experimental and simulator results for waterflood of decane in Berea rock at various concentrations of the anionic surfactant, ethoxy sulphate is shown in Table 5.

The history match of oil recovery, pressure drop and the resulting relative permeability curves obtained from the simulator for this system for different anionic surfactant concentrations are shown in the Figures A11-A15 of Appendix. Figure 5 shows the effect of anionic surfactant concentration on oil recovery, pressure drop, relative permeability ratio and fractional water flow.

From Table 5, it is evident that only minor adjustments are needed in end-point water relative permeabilities in the simulator to obtain acceptable history match of oil recovery and pressure drop at all anionic surfactant concentrations used in this study

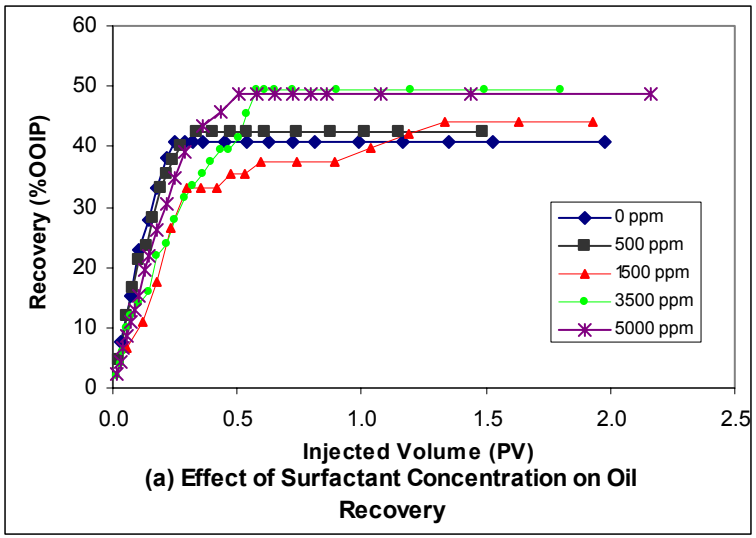
Relative permeability curves at 0 ppm surfactant concentration (Figure A11(c)) indicate water-wet / intermediate-wet characteristics (S_{wi} = 40% > 25%, $S_{w,c-o}$ = 50%, K_{rw} = 20% < 30%). The end-point oil relative permeability of 76% at S_{wi} is caused by emulsion formation.

Relative permeability curves at 500 ppm surfactant concentration (Figure A12(c)) indicate weakly water-wet / intermediate-wet characteristics (S_{wi} = 36% > 25%, $S_{w,c-o}$ = 48% < 50%, K_{rw} = 25% < 30%). The end-point oil relative permeability of 67% at S_{wi} is once again attributed to emulsion formation.

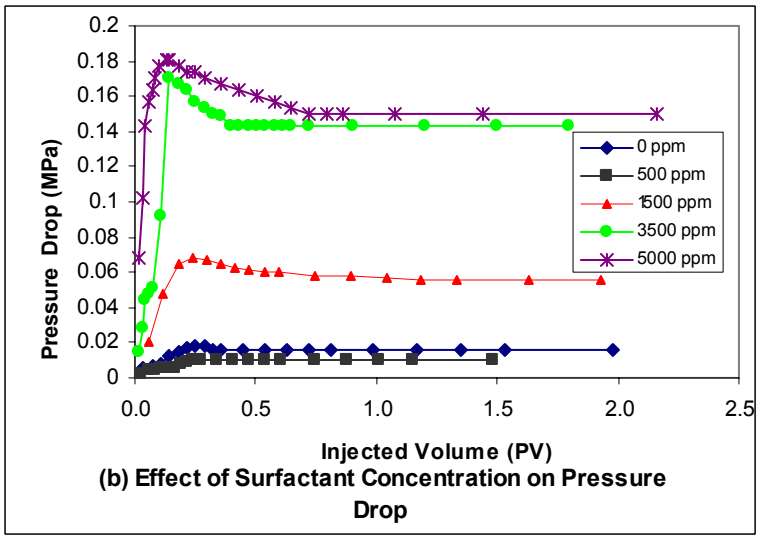
Similar trends are observed in the characteristics of relative permeability curves at other surfactant concentrations.

Table 5: Comparison between the Experimental and Simulator Results for waterflood of Decane in Berea Core at Various Anionic Surfactant Concentrations

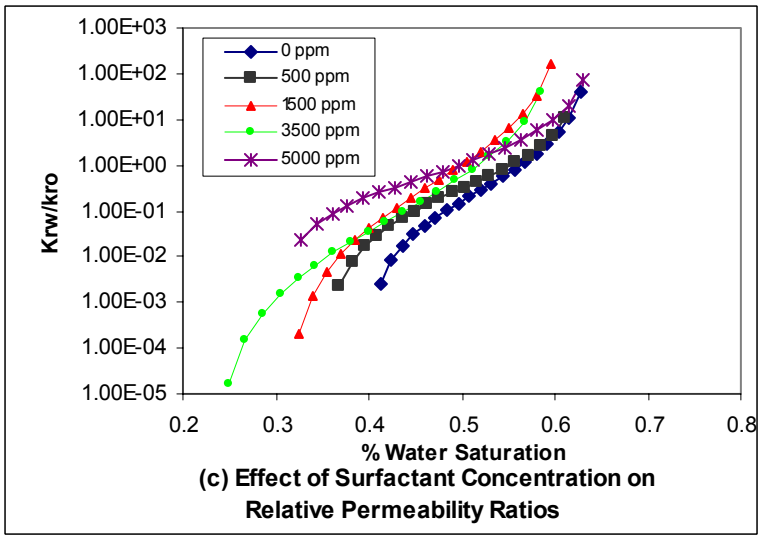
Case	**Experimental**					**Simulator**			
	Recovery (%OOIP)	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**
Brine	40	0.400	0.374	0.757	0.1417	0.400	0.360	0.757	0.2020
500 ppm	42	0.355	0.390	0.667	0.1434	0.355	0.375	0.667	0.2450
1500 ppm	45	0.310	0.400	0.211	0.1645	0.310	0.390	0.211	0.2430
3500 ppm	49	0.230	0.410	0.038	0.0322	0.230	0.400	0.038	0.0047
5000 ppm	49	0.310	0.360	0.019	0.0150	0.310	0.360	0.019	0.0090



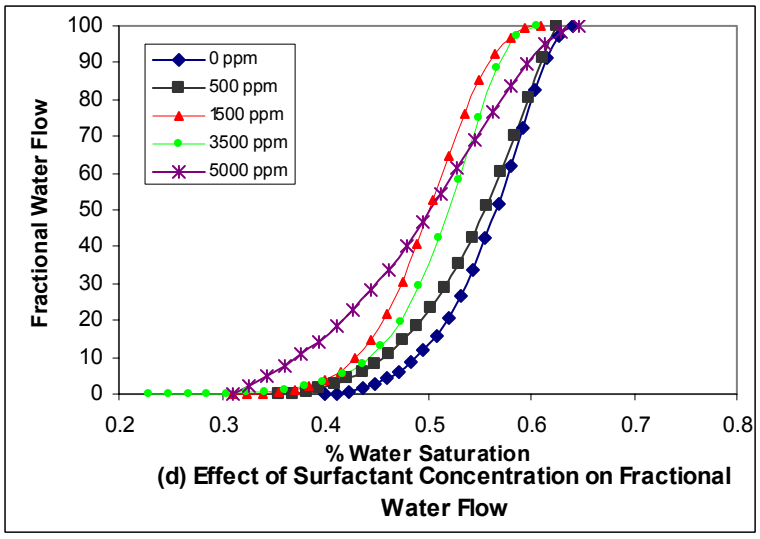
(a) Effect of Surfactant Concentration on Oil Recovery



(b) Effect of Surfactant Concentration on Pressure Drop



(c) Effect of Surfactant Concentration on Relative Permeability Ratios



(d) Effect of Surfactant Concentration on Fractional Water Flow

Figure 5: Coreflood Simulator Results for waterflood of Decane in Berea Rock at Various Anionic Surfactant Concentrations

The important observations made from the experimental results are:

1) The oil recovery increases from 40% to 49% as the anionic surfactant concentration is increased from 0 ppm to 5000 ppm. These improvements in oil recoveries are mainly due to reduction in oil-water interfacial tension by the surfactant and not to wettability change as discussed below.
2) Initial water saturation decreases from 40% to 31% in these floods as the anionic surfactant concentration is increased from 0 ppm to 5000 ppm. Thus, the initial water saturation is always greater than 30% for all these floods, indicating water-wet characteristics according to Craig's rules.
3) The end-point relative permeability to water at residual oil saturation decreases from 25% to 0.9% as the anionic surfactant concentration increases from 0 ppm to 5000 ppm. It is always less than 30% of the end-point oil relative permeability for all these floods, suggesting water-wet characteristics.
4) The crossover-point shifts to the left from 55% to 40% as the anionic surfactant concentration increases from 0 ppm to 5000 ppm. This indicates a shift from water-wet to less water-wet or intermediate-wet condition as the surfactant concentration is increased. However, this shift is attributed to oil/water emulsions and not to wettability changes (i.e., it is a viscosity rather than wettability effect).
5) The end-point relative permeability to oil at initial water saturation decreases from 76% to 2% as the anionic surfactant concentration increases from 0 ppm to 5000 ppm. This drop is attributed to high pressure-drops caused by the oil/water emulsion.

6) The relative permeability ratio curves shift to the left as the anionic surfactant concentration increased. Although, this appears to indicate a shift from water-wet to less water-wet or intermediate-wet condition, this shift is attributed to oil/water emulsion.

In summary, the first two of Craig's criteria indicate no wettability effects in the decane case while the latter criteria cannot be used to infer wettability as they are affected by the oil-water emulsion. It can be concluded that the system of Berea rock + Yates synthetic brine + decane is non-reactive and neutral to wettability alterations even in the presence of anionic surfactant. For further verification, experimentation is suggested to measure contact angles on Berea rock + Yates synthetic brine + decane system at various anionic surfactant concentrations, using the DDDC technique.

The chart of recovery versus injected volume (Figure 5(a)) indicates that the recovery gradually increases as the anionic surfactant concentration is increased from 0 ppm to 5000 ppm. However, there is a significant increase in the recovery (49%) at 3500 ppm anionic surfactant concentration. Above 3500 ppm surfactant concentration, the increase in recovery is small, suggesting that 3500 ppm surfactant concentration is the optimum for this system to maximize oil recovery.

The pressure drop gradually increases as the anionic surfactant concentration is increased (Figure 5(b)). This is attributed mainly to oil/water emulsions. At higher anionic surfactant concentrations, oil/water emulsions were much stronger, causing high pressure drops and lower end-point oil relative permeabilities.

4.2.2 Reactive System (Berea Rock + Yates Synthetic Brine + Yates Crude Oil):

Strong oil/water emulsion was observed during the tests even in this reactive system. No 5000 ppm surfactant flood was conducted for this system due to the formation of a very strong emulsion at a surfactant concentration of 3500 ppm. Figure 6 shows the picture of oil/water emulsion observed during the coreflooding experiments in this system.

The summary of experimental and simulator results for waterflood of Yates crude oil in Berea rock at various concentrations of the anionic surfactant, ethoxy sulphate is shown in Table 6.

The history match of oil recovery, pressure drop and the resulting relative permeability curves obtained from the simulator for this system for different anionic surfactant concentrations are shown in the Figures A16-A19 of Appendix. Figure 7 presents the effect of anionic surfactant concentration on oil recovery, pressure drop, relative permeability ratio and fractional water flow.

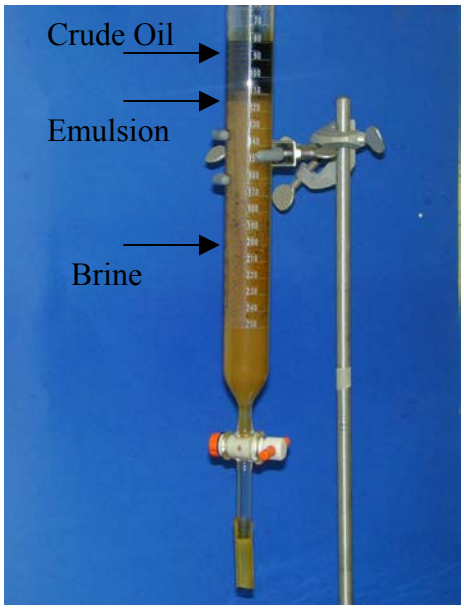


Figure 6: Picture Showing Oil / Water Emulsion

Only minor adjustments are done in end-point water relative permeabilities in the simulator to obtain acceptable history match of oil recovery and pressure drop at all anionic surfactant concentrations used in this study (Table 6).

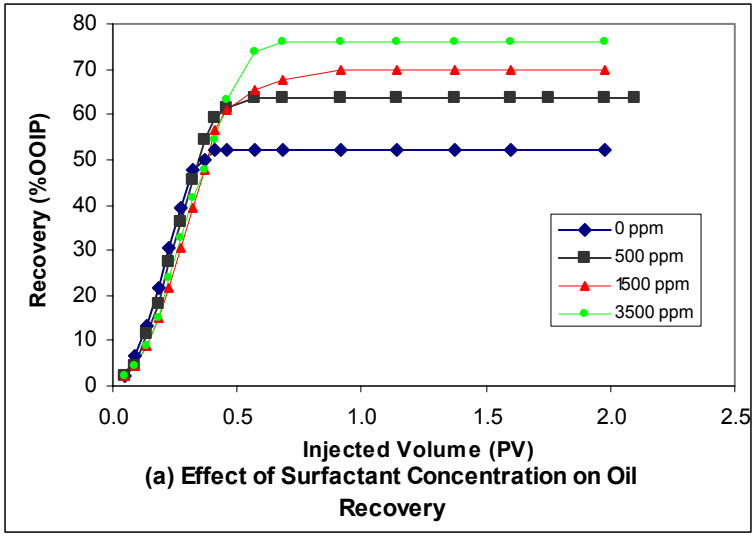
Relative permeability curves at 0 ppm surfactant concentration (Figure A16(c)) indicate water-wet characteristics (S_{wi} = 30% > 25%, $S_{w,c-o}$ = 55% > 50%, K_{rw} = 4.0% < 30% and K_{ro} = 97 % > 95%)..

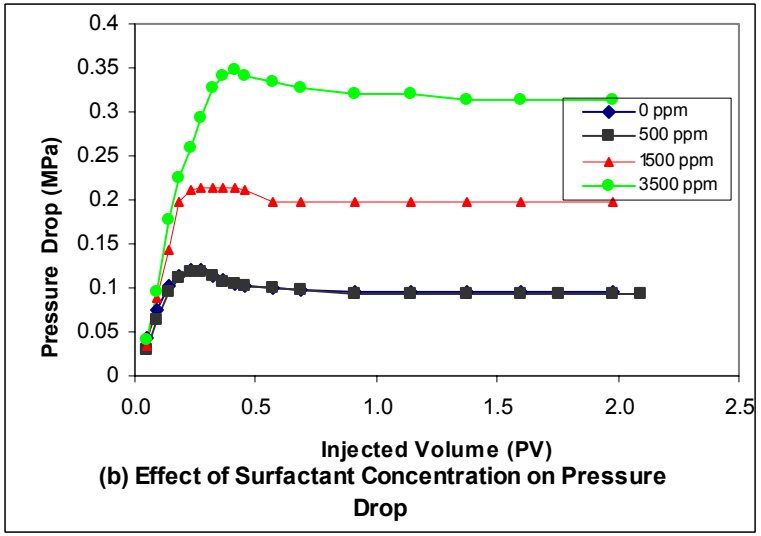
Relative permeability curves at 500 ppm surfactant concentration (Figure A17(c)) indicate strong water-wet characteristics (S_{wi} = 33% > 25%, $S_{w,c-o}$ = 60% > 50%, K_{rw} = 4.5% < 30%). However, the decrease in K_{ro} to 86% for this particular rock-fluids system is attributed to wettability alteration instead of emulsion due to the reasons discussed below.

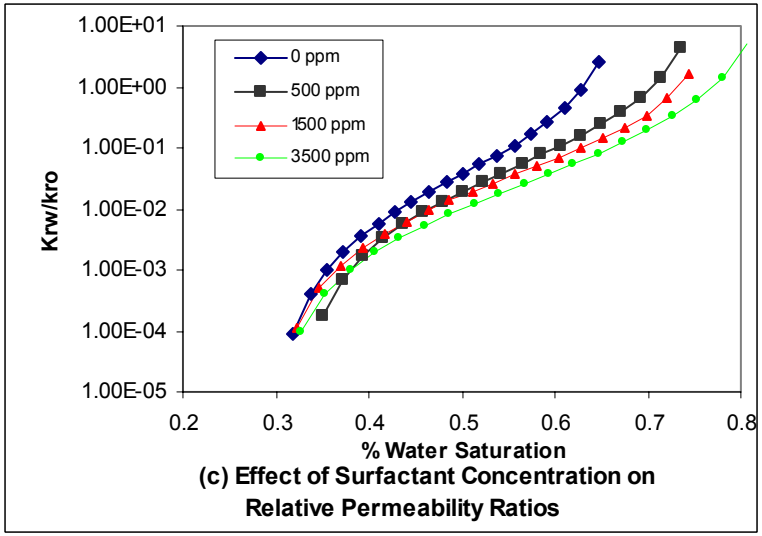
Similar trends are observed in all these characteristics of relative permeability curves even at higher anionic surfactant concentrations.

Table 6: Comparison between the Experimental and Simulator Results for waterflood of Yates Crude Oil in Berea Core at Various Anionic Surfactant Concentrations

Case	**Experimental**					**Simulator**			
	Recovery (%OOIP)	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**	**S_{wi}**	**S_{or}**	**K_{ro}**	**K_{rw}**
Brine	52	0.300	0.350	0.967	0.0537	0.300	0.340	0.967	0.0417
500 ppm	62	0.330	0.260	0.860	0.0860	0.330	0.250	0.860	0.0451
1500 ppm	70	0.300	0.230	0.451	0.0268	0.300	0.230	0.451	0.0215
3500 ppm	78	0.300	0.180	0.451	0.0182	0.300	0.170	0.451	0.0140







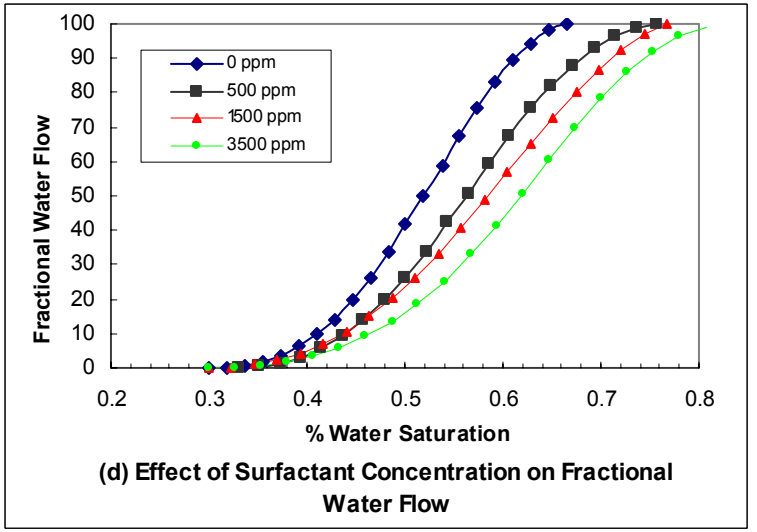


Figure 7: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Rock at Various Anionic Surfactant Concentrations.

The experimental results lead to the following observations.

1) Oil recovery increases from 52% to 78% is observed as the anionic surfactant concentration increases from 0 ppm to 3500 ppm.
2) The initial water saturations and end-point water relative permeabilities are nearly constant in all the floods.
3) The water saturation at crossover-point shifts from 55% to 70% as the surfactant concentration increases from 0 ppm to 3500 ppm.
4) The end-point oil relative permeability decreases from 97% at 0 ppm to 86% at 500 ppm then further decreases to 45% at 1500 ppm. Further increase of anionic surfactant concentration to 3500 ppm does not change the end-point oil relative permeability. This drop in end-point oil permeabilities is attributed to oil/water emulsions, which were visible in the collected production streams.
5) The relative permeability ratio curves shift to the right as the anionic surfactant concentration increases from 0 ppm to 3500 ppm. This is mostly due to alteration of wettability to mixed-wet condition as discussed below.

The formation of oil/water emulsion has a profound influence on end-point oil relative permeabilities as discussed in sections 4.1.1 and 4.2.1. This effect was demonstrated in the relative permeability ratio plots in these sections (Figures 3(c) and 5(c)) where the curves are shifting to the left as the surfactant concentration is increased. However, for this particular reactive system of Berea rock + Yates synthetic brine + Yates crude oil, in spite of emulsion formation, the relative permeability ratio curves are shifting to the right as the surfactant concentration is increased. This is quite similar to the characteristics exhibited by the nonionic surfactant with the same rock-fluids system.

The relative shifts in the relative permeability ratio curves in this system are not as large as those observed in the case of nonionic surfactant (Figures 4(c) and 7(c)), which did not form oil/water emulsions. This smaller change in relative permeability ratio curves for the anionic surfactant is caused by the competing effects of (1) formation of oil/water emulsion (which shifts the relative permeability ratio curves to the left) and (2) the development of mixed-wettability (which shifts the relative permeability ratio curves to the right). However, the rightward shift (Figure 7(c)) for this particular reactive system clearly demonstrates that the wettability alteration to mixed-wet outweighs the effect of the emulsions. Thus, this particular case confirms wettability shifts by the surfactants in the rock-fluids systems with Yates crude oil.

The same discussion in section 4.1.2 for the development of mixed-wettability due to the presence of nonionic surfactant (ethoxy alcohol) in the reactive system of Berea rock + Yates synthetic brine + Yates crude oil holds good even for this reactive system in the presence of anionic surfactant (ethoxy sulphate). Development of mixed-wettability condition at higher anionic surfactant concentrations could be verified by measuring the contact angles on Berea rock + Yates synthetic brine + Yates crude oil system.

Recovery increase at 3500 ppm anionic surfactant concentration is 78% compared to 52% at 0 ppm (Figure 7 (a)). Above 3500 ppm surfactant concentration, the increase in oil recovery is small, suggesting that 3500 ppm surfactant concentration is the optimum for this system. Furthermore, the recoveries are much higher in the reactive system compared to the recoveries in the non-reactive system (at the same surfactant concentration). This substantiates that the Berea rock + Yates synthetic brine + decane

system is non-reactive and does not under go wettability alterations. The significant increase in oil recovery in the reactive system is attributed to wettability alteration.

The pressure drop gradually increases as the anionic surfactant concentration is increased (Figure 7(b)). This is attributed to the oil/water emulsions observed in this reactive system. The oil/water emulsions were so strong that 5000 ppm flood with the anionic surfactant was not possible with the available equipment.

4.3 Effect of IFT and Wettability on Oil Recovery

The recoveries at each nonionic and anionic surfactant concentrations in the reactive system are significantly higher than the recoveries at the same nonionic and anionic surfactant concentrations in the non-reactive system (Figures 8 and 9).

The oil recovery as observed in this study would be associated with four to five orders of magnitude reduction in the interfacial tension if there were no wettability alteration. However, interfacial tension reduction with these surfactants is only of two orders of magnitude (from 28 dynes/cm to 0.21 dynes/cm)[78].

Therefore, improvements in oil recovery observed in this study are attributed to wettability alteration rather than interfacial tension reduction.

In spite of relatively adverse mobility ratio for crude oil compared to that for decane (M = 0.940 for crude oil versus M = 0.111 for decane), the oil recovery in Yates crude oil system is higher than decane system at 0 ppm surfactant concentration. This was due to lower interfacial tension (19 dynes/cm of Yates crude oil / Yates synthetic brine versus 52 dynes/cm of decane / Yates synthetic brine) and higher contact angle (102^0 of Yates crude oil / Yates synthetic brine on Berea versus 57^0 of decane / Yates synthetic brine on Berea). The adhesion tension ($\sigma\cos\theta$) for these two cases differs

markedly from 28.32 dynes/cm for decane to – 3.95 dynes/cm for the crude oil. This large change in the adhesion tension has overshadowed the effect of adverse mobility ratio, yielding higher oil recoveries in the crude oil system at 0 ppm in both the Figures 7 & 8.

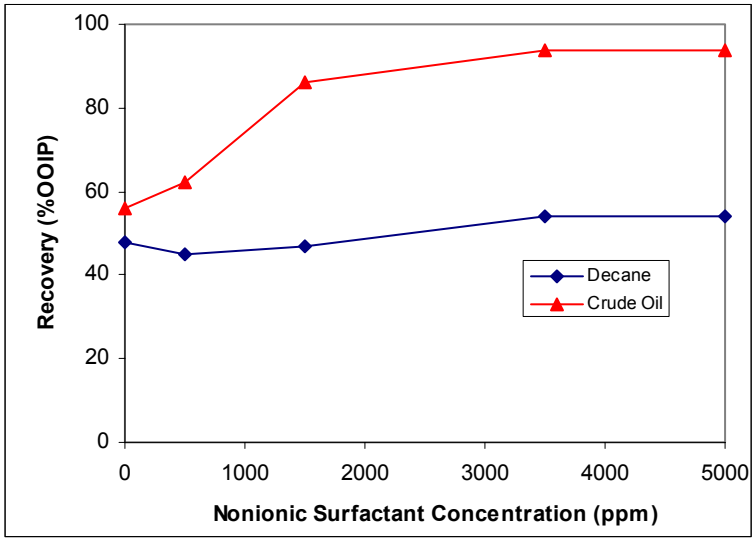


Figure 8**:** Effect of Nonionic Surfactant Concentration on Oil Recovery

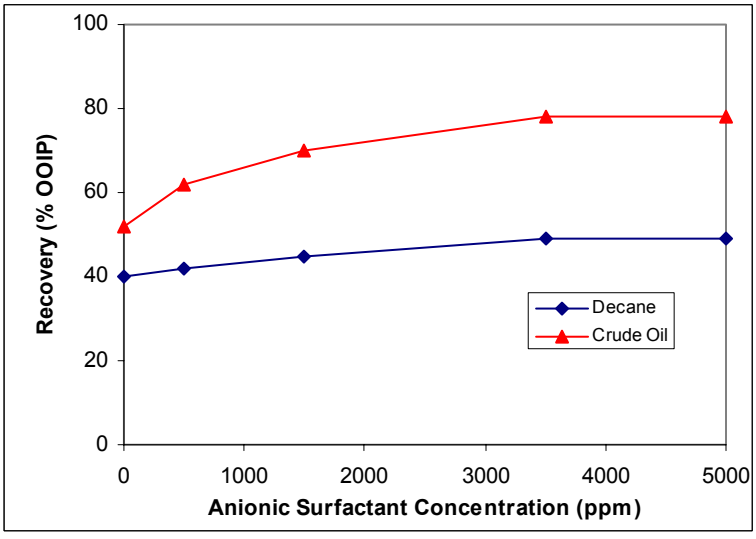


Figure 9**:** Effect of Anionic Surfactant Concentration on Oil Recovery

4.4 Optimum Surfactant Type and Concentration

The recoveries for the nonionic surfactant (ethoxy alcohol) concentrations are higher than the recoveries at the same concentrations of the anionic surfactant (ethoxy sulphate) (Figures 4(a) and 7(a)). Optimum oil recovery is obtained at a surfactant concentration of 3500 ppm for both nonionic and anionic surfactants. Nonionic surfactant did not form emulsion in Yates crude oil while the anionic surfactant caused flow problems due to the formation of strong emulsion. These observations suggest that the nonionic surfactant, ethoxy alcohol as the preferred surfactant and 3500 ppm as the optimum surfactant concentration.

4.5 Mixed-Wettability

The concept of mixed-wettability is proposed by Salathiel[76] in 1973 to explain the abnormally high oil recoveries in Woodbine floods (East Texas). In mixed-wettability condition, the finer pores and grain contacts are water-wet and the surfaces of larger pores are strongly oil-wet. If these oil-wet paths were continuous through the rock, water would displace oil from the larger pores so that the capillary forces would hold little or no oil in smaller pores or at grain contacts.

Salathiel postulated the development of mixed-wettability with the following explanation. As oil accumulates in a reservoir, water present in the initially water-wet rock is displaced from the larger pores while the capillary pressure retains water in smaller pores and at grain contacts. After extended periods of time, some organic materials from the oil may deposit on to those rock surfaces that are in direct contact with oil, making those surfaces strongly oil-wet. This phenomenon leads to the development

of so called mixed-wettability. The development of mixed-wettability condition as postulated by Salathiel is shown in Figure 10 (taken from reference 76).

It is obvious from the literature[65,75,76] that a steady increase in initial water saturation, higher oil recoveries, lower residual oil saturations and shift to the right in the relative permeability ratio curves are the clear indications for the development of mixed-wettability.

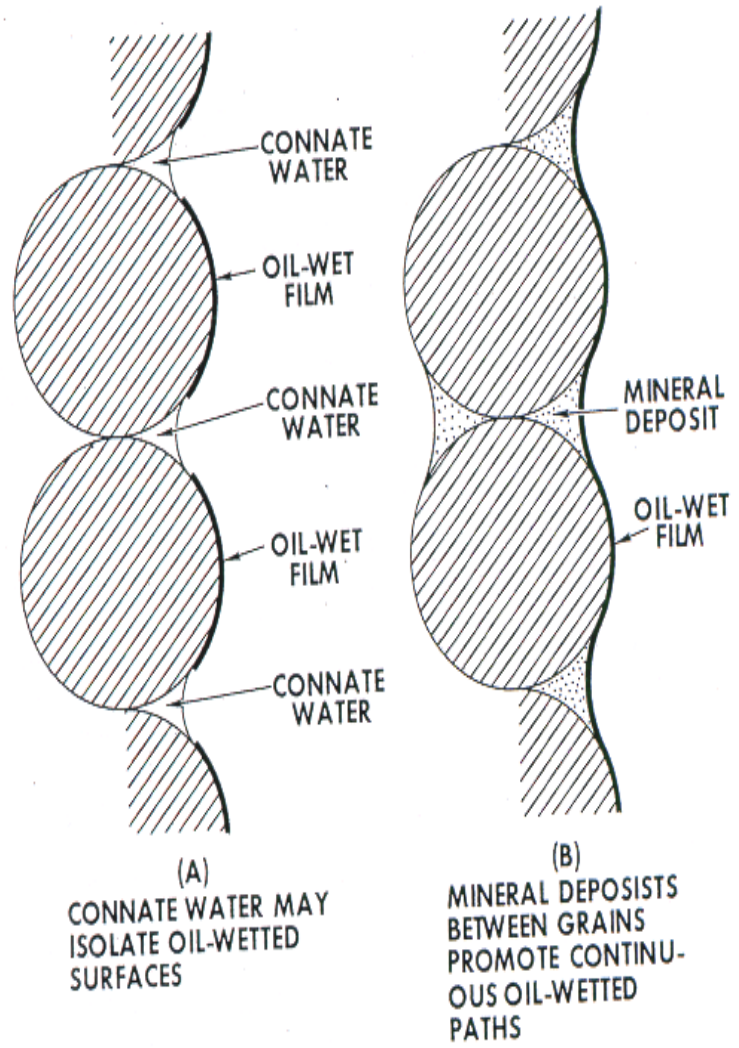


Figure 10: Development of Mixed-Wettability as Postulated by Salathiel[76]

4.6 Proposed Mechanisms for Wettability Alteration by Surfactants

The reactive system of Brea rock + Yates synthetic brine + Yates crude oil is water-wet in the absence of the surfactants and gradually shifts to mixed-wet as the surfactant concentration is increased. Mixed wettability has a more pronounced influence on waterflood oil recovery than the changes in the characteristics of relative permeability curves[65]. The possible mechanisms responsible for the development of mixed-wet condition are discussed below.

4.6.1 Thin Water Film Stability[77]

If the system is water-wet, the rock surface is covered with water and oil exists in the form of globules in the middle of bigger pores. There is a film of water between the rock surface and oil globules. In the presence of a water-soluble surfactant, this thin liquid film becomes unstable due to adsorption of surfactant molecules at the rock-water interface and the orientation of surfactant molecules at these interfaces. The instability of the thin water film at the interface leads to oil/rock interactions and the formation of a continuous oil-wet path for displacement of oil. This is the development of mixed-wettability[76].

4.6.2 Surfactant Orientation[22]

Surfactants are amphipolar or amphipathic molecules composed of a hydrophilic head and a hydrophobic tail group. This dual nature of surfactants produces a strong affinity for interfaces between immiscible fluids such as oil and water. A surfactant that orients itself on a solid surface such that the surfactant molecules have the hydrophobic tail groups away from the surface or along the surface can make the surface oil-wet. This results in the formation of a continuous oil-wet path for favorable displacement of oil,

present in the bigger pores of a water-wet system. As mentioned earlier, this is nothing but the development of mixed wettability, as envisioned by Salathiel[76].

4.7 Preliminary Economic Considerations

The following material balance calculations are performed for the optimum surfactant type and concentration obtained in the present study to examine the preliminary economic feasibility of a surfactant flood in the field. For detailed economic calculations, reservoir simulation studies incorporating parameters like production profile, incremental production, production rate, surfactant concentration, savings in produced water handling will be required.

Let us consider the application of the surfactant flood to a shallow sandstone reservoir having the following properties.

A = 20- acre spacing, five-spot pattern

h = 20 ft

ϕ = 20 %

S_{orw} = 30 %

S_{orc} = 4 %

S_{oi} = 70 %

B_{oi} = 1.05 bbl / STB

L = distance between the injector and producer

$= \sqrt{(20 acres)(43560 sqft/acre)/2}$

= 660 ft

$$M = \frac{k_{rw}/\mu_w}{K_{ro}/\mu_o}$$

$$= \frac{(0.1322/1.0)}{(1.0/12.8)}$$

$$= 1.70$$

From the Figure 4.5 of Green & Willhite[1], at one pore volume of water injected and at a mobility ratio of 1.7,

Areal sweep efficiency $= E_A = 0.85$

Darcy Velocity = u = 0.02 ft/day = 0.02 ft/D $\left(\frac{1}{5.615\, ft^3/bbl}\right)$

$$= 0.0035618 \text{ B/D-ft}^2$$

Viscous to gravity ratio $R_{v/g} = \frac{2050u(B/D.ft^2)\mu_d(cp)L(ft)}{k(md)\Delta\rho(gm/cc)h(ft)}$

$$= \frac{2050 \times 0.0035618 \times 12.8 \times 660}{400 \times (1.0 - 0.874) \times 20}$$

$$= 61.0$$

From the Figure 4.17 of Green & Willhite[1], at a $R_{v/g}$ of 61.0 and a mobility ratio of 1.7,

Vertical sweep efficiency $= E_H = 0.70$

Volumetric sweep efficiency $= E_V = E_A \times E_H$

$$= (0.85)\ (0.70)$$

$$= 0.60$$

Microscopic displacement efficiency $= E_D = 0.94$

Overall efficiency $= E = E_D \times E_V = 0.564$

Pore volume $= V_p = Ah\phi$

$= 20 \text{ acres} \times 43560 \text{ ft}^2 / \text{acre} \times 20 \text{ ft} \times 0.20 \times 0.17809 \text{ bbl} / \text{ft}^3$

$= 620{,}624 \text{ bbl.}$

Initial oil in place $= N = Ah\phi S_{oi} / B_{oi}$

$= (20 \text{ acres} \times 43560 \text{ ft}^2 / \text{acre} \times 20 \text{ ft} \times 0.20 \times 0.70 \times 0.17809 \text{ bbl} / \text{ft}^3) / (1.05)$

$= 413{,}749 \text{ STB.}$

Oil recovery due to waterflood

$= (20 \times 43560 \times 20 \times 0.20 \times (0.70 - 0.30) \times 0.564 \times 0.17809) / (1.05)$

$= 133346 \text{ STB}$

The combined oil recovery by waterflooding and surfactant process

$= (20 \times 43560 \times 20 \times 0.20 \times (0.70 - 0.04) \times 0.564 \times 0.17809) / (1.05)$

$= 220020 \text{ STB.}$

The incremental oil recovery due to surfactant flood

$= (220020 - 133346)$

$= 86674 \text{ STB.}$

The key variable affecting the economics of enhancing oil recovery using a low concentration of surfactant is the cost of injecting surfactant. This cost includes those associated with facilities, operating expenses and the surfactant.

Let us assume that one pore-volume of water is injected at an optimum surfactant concentration of 3500 ppm to achieve this incremental oil recovery.

Surfactant consumption

$= (620{,}624 \text{ bbl}) \times (159 \text{ liters} / \text{bbl}) \times (3500 \text{ mg} / \text{liter}) \times (10^{-6} \text{ kg/mg})$

$= (345{,}377.256 \text{ kgs}) \times (2.2046 \text{ lbs} / \text{kg})$

$= 761{,}430.5 \text{ lbs}$

Oil price = $ 30 per bbl

Income from to additional oil recovery due to surfactant flood,

$$= (86674) \times (\$30) = \$2{,}600{,}220.$$

This surfactant is readily soluble in water with minimal mixing. Therefore, it is reasonable to assume that facilities and operating expenses are negligible.

Surfactant costs vary from $0.50 to $2.00 per lb[44] and an average surfactant cost of $1.25 per lb is used, which is very close to the value used by Spinler et al.[45],

Surfactant cost = $(761430.5) \times (1.25)$

$$= \$951{,}788.$$

Profit = $(2600220 – 951788)

$$= \$1{,}648{,}432.$$

Net profit per bbl of incremental oil

$$= 1648432 / 86674$$

$$= \$19.00 \text{ per bbl.}$$

The preliminary cost analysis indicates positive economics for enhanced oil recovery through surfactant-induced wettability alteration. Further work using a reservoir simulator for specific reservoirs is needed for field implementation.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of Findings and Conclusions

Coreflooding experiments are conducted in this study on two types of systems namely non-reactive (Berea Rock + Yates Synthetic brine + decane) and reactive (Berea rock + Yates synthetic brine + Yates crude oil) at various concentrations of nonionic (ethoxy alcohol) and anionic (ethoxy sulphate) surfactants. In addition to quantifying the enhancement in oil recovery, oil-water relative permeabilities are also estimated using a coreflood simulator by history matching the recovery and the pressure drop data obtained from the dynamic displacements. The relative permeability variations are interpreted using Craig's rules-of-thumb[71] to characterize the wettability alterations induced by the surfactants.

The salient findings from this experimental study are:

1. Both nonionic and anionic surfactants are effective in enhancing the oil recovery in Berea cores containing decane and Yates crude oil as the oleic phases and Yates synthetic brine as the aqueous phase. The nonionic surfactant resulted in an increase in oil recovery from 48% (at 0 ppm surfactant) to 54% (at 3500 ppm surfactant) for the decane system. This increase is higher (from 56% to 94%) with the Yates crude oil. Similar trends are observed with the anionic surfactant: oil recovery increased from 40% (at 0 ppm surfactant) to 49% (at 3500 ppm surfactant) for the decane system and from 52% to 78% in the Yates crude oil system.

   For all the four cases studied, the maximum oil recovery is obtained at a surfactant concentration of 3500 ppm. Nonionic surfactant is more effective than anionic

surfactant due to higher oil recovery (almost double) and the absence of emulsions. Anionic surfactant caused severe emulsion problems. The nonionic surfactant at 3500 ppm concentration is recommended as the optimum.

2. The two main mechanisms responsible for enhanced oil recovery with surfactants are reduction in oil-water interfacial tension and wettability alteration. The higher incremental oil recoveries by the surfactants in the reactive system compared to those in the non-reactive system indicate that controlling mechanism for enhanced oil recovery is wettability alteration rather than the reduction in interfacial tension. The marginal incremental recoveries in the decane systems could be attributed to reduction in interfacial tension by only about two orders of magnitude.
3. The enhancements in oil recovery in Yates crude oil system are attributed to the mixed-wettability condition. The development of mixed-wettability is supported by the shift to the right in relative permeability ratio plots. Strong oil-water emulsions are observed in three of four systems examined. The emulsions affected the pressure drop during the waterfloods, which in turn affected the end-point oil relative permeabilities and cross-over point saturations. Therefore, in cases where emulsions formed, Craig's rules could not be used to infer wettability changes. Another limitation to the applicability of Craig's rules is that it is not possible to infer the development of mixed-wettability condition from these rules as observed in this study because these rules are used only to distinguish between strongly water-wet and oil-wet systems.
4. The main possible mechanisms responsible for the development of mixed-wettability observed in this study are (1) the instability of the thin wetting water film on the rock surface in the presence of water-soluble surfactants and (2) the orientation of

surfactant molecules with their hydrophobic tail groups away from the solid surface or along the solid surface, rendering an oil-wet characteristics.

5. The preliminary economic calculations based on optimum parameters obtained in this study show that the surfactant-induced wettability alteration process is profitable at an over all sweep efficiency of 56% and a crude oil price of $30 per barrel. A net profit of $19 per barrel of incremental oil recovery is obtained, indicating that this process is economically feasible and can compete with other enhanced oil recovery methods.

5.2 Recommendations for Future Work

In the present study, Craig's rules of thumb[71] were used to characterize the wettability alterations through surfactant-induced relative permeability modifications. However, the relative permeabilities are the composite effect of pore geometry, wettability, surface tension, fluid distribution and saturation history. Hence for better understanding of the wettability alterations induced by the surfactants, the contact angles should be measured in non-reactive and reactive systems at various concentrations of nonionic and anionic surfactants.

Furthermore, contact angle measurements for Yates reservoir fluids and decane on smooth, polished surfaces such as glass or quartz at various nonionic and anionic surfactant concentrations would clarify the effect of surface roughness on wettability alterations induced by these surfactants.

Reservoir condition tests could confirm the wettability shifts caused by these surfactants at actual operating conditions in the field. A detailed economic analysis using reservoir simulators is needed to check the feasibility of this process in the field.

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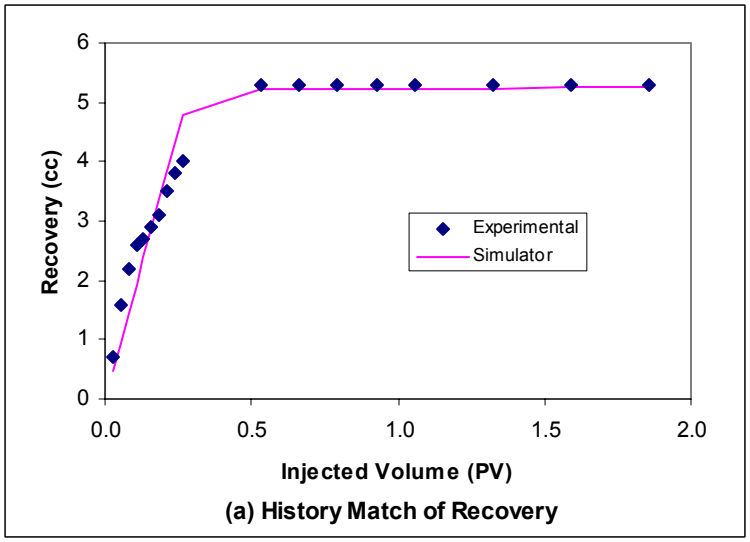
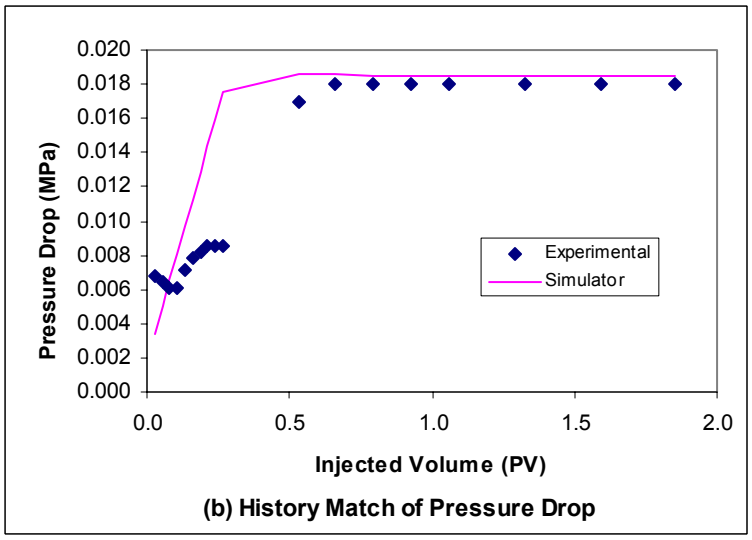
APPENDIX: HISTORY MATCH OF RECOVERY, PRESSURE DROP AND RESULTING RELATIVE PERMEABILITIES FROM SIMULATOR





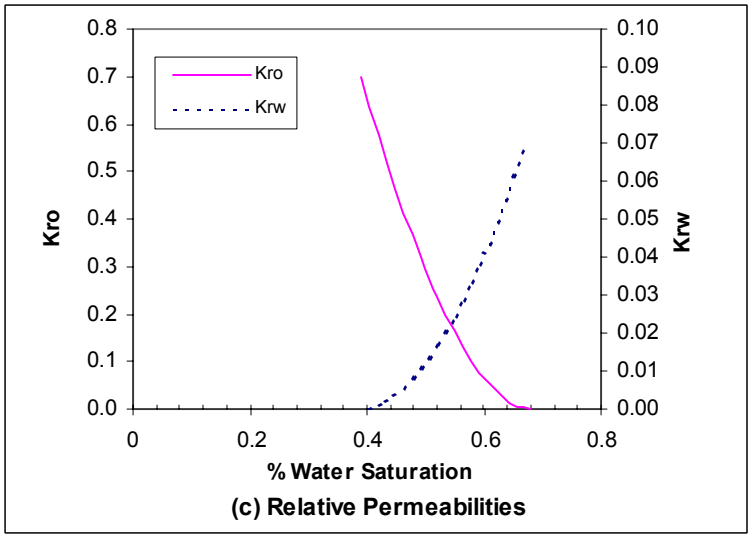
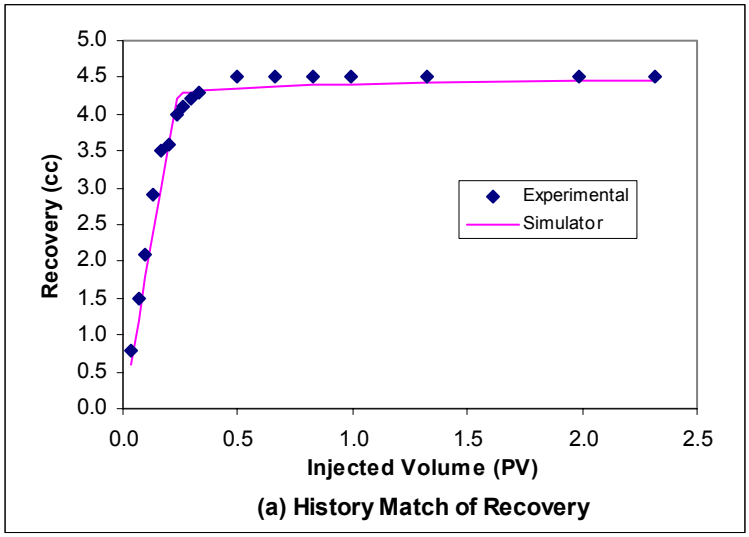
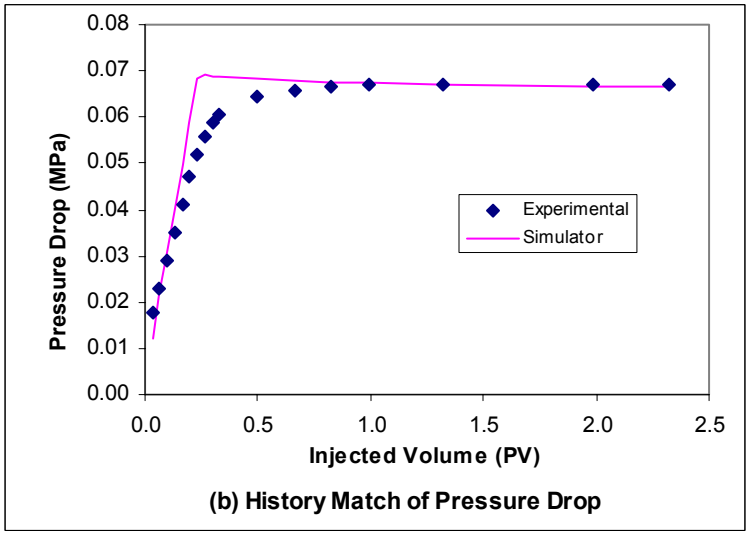


Figure A1: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Nonionic Surfactant Concentration of 0 ppm





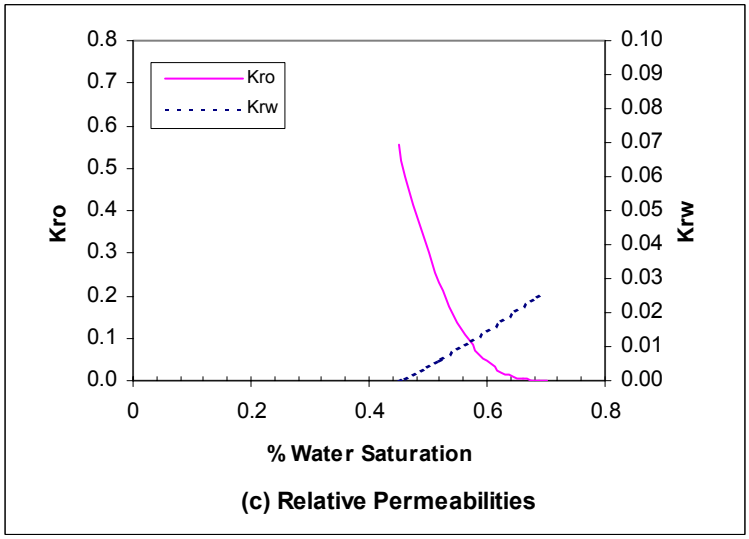


Figure A2: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Nonionic Surfactant Concentration of 500 ppm

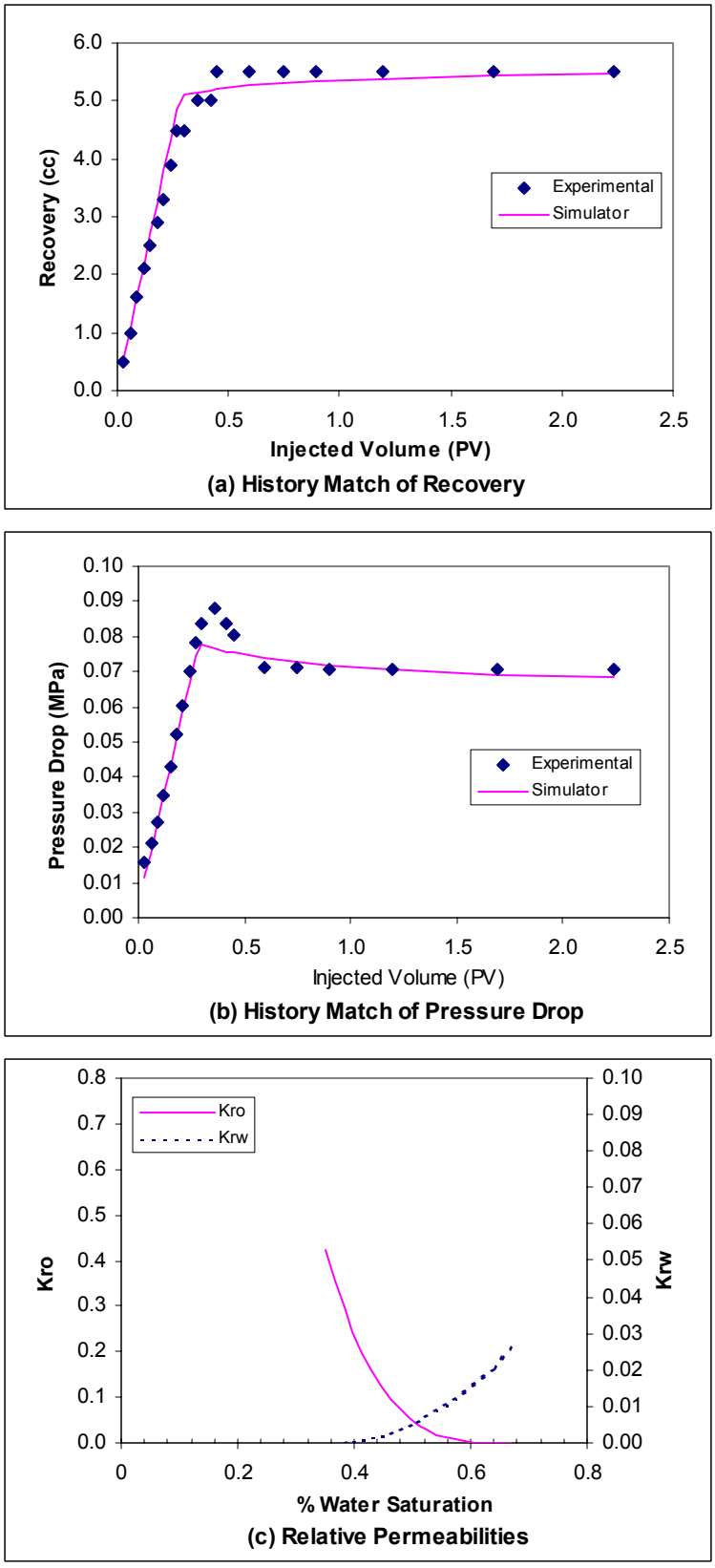
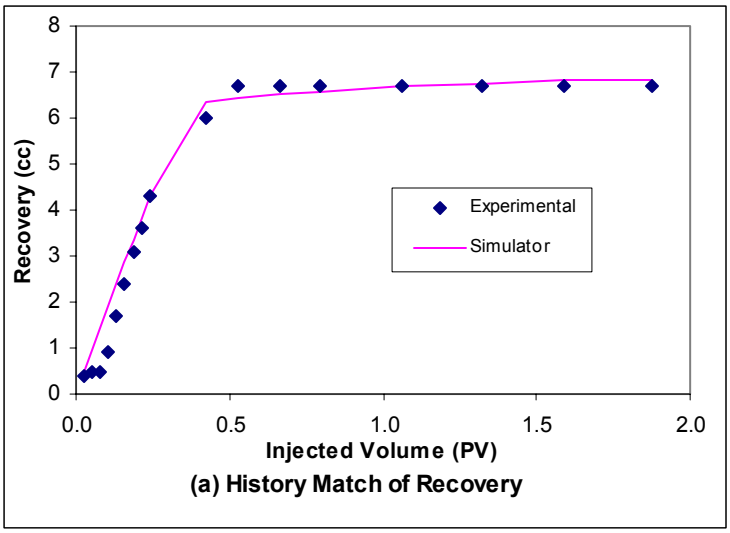
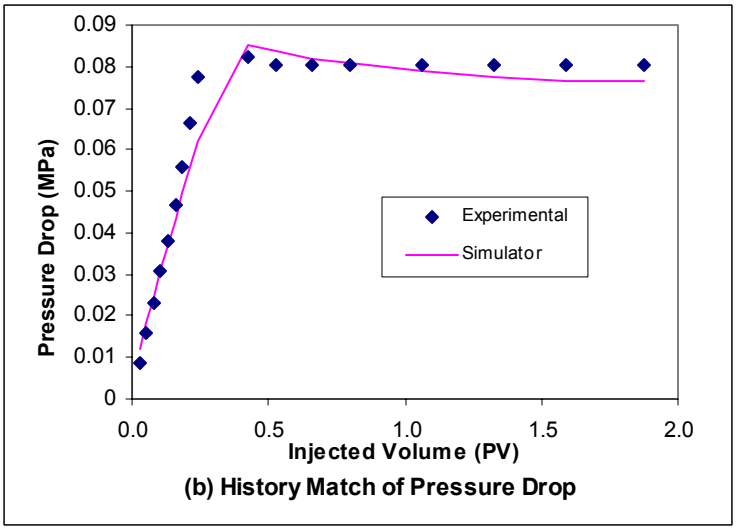


Figure A3: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Nonionic Surfactant Concentration of 1500 ppm





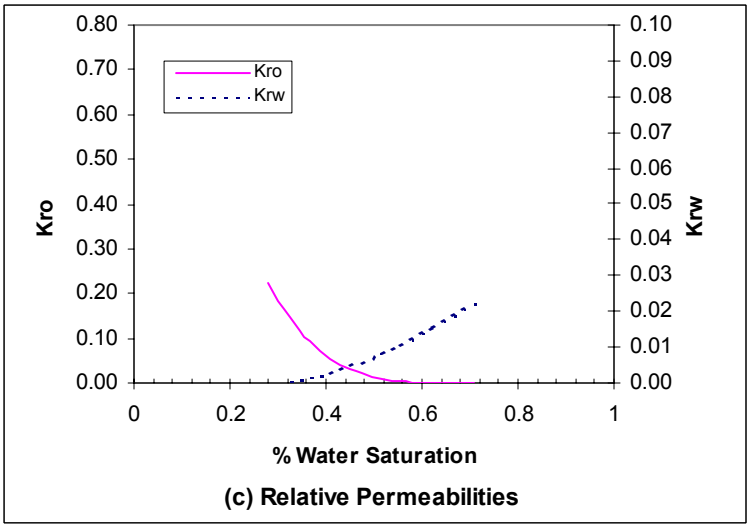
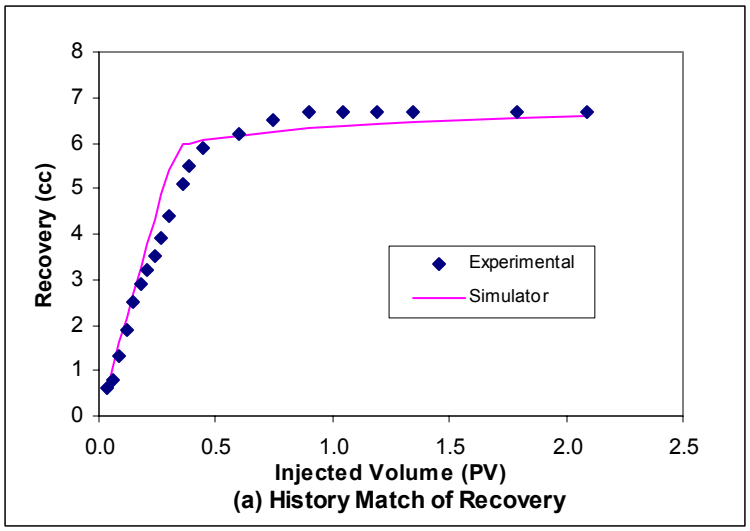
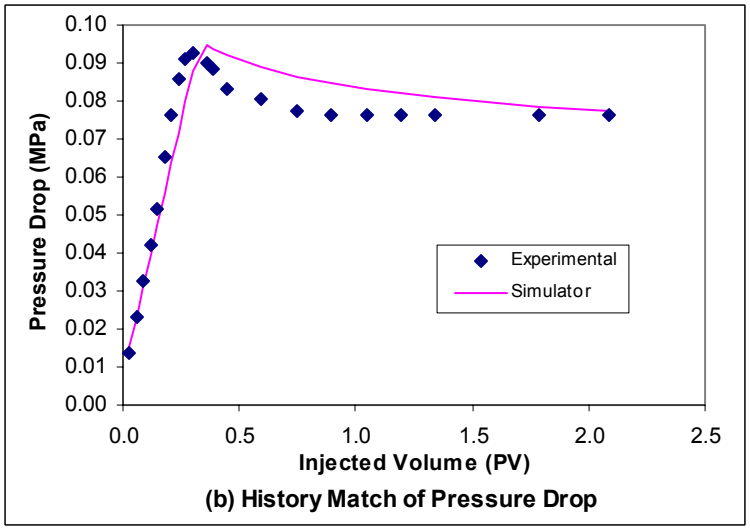


Figure A4: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Nonionic Surfactant Concentration of 3500 ppm





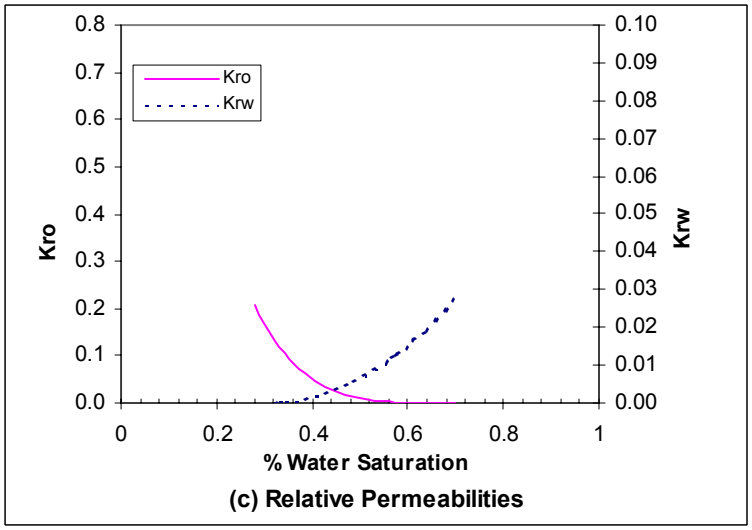
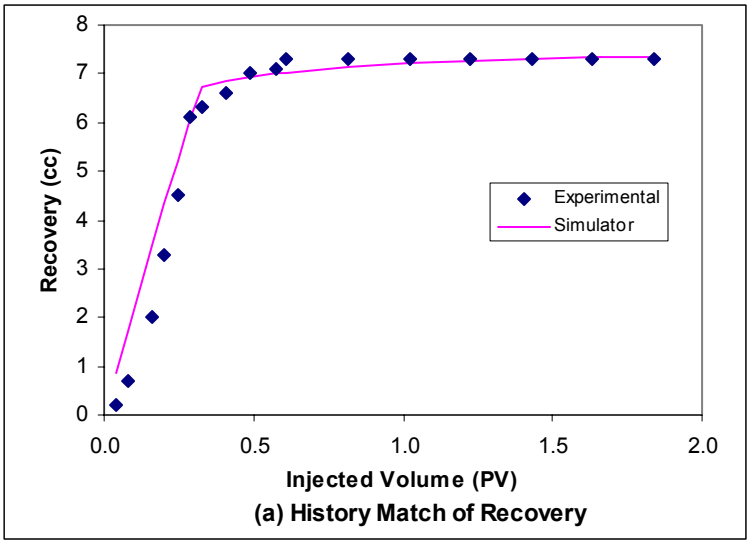
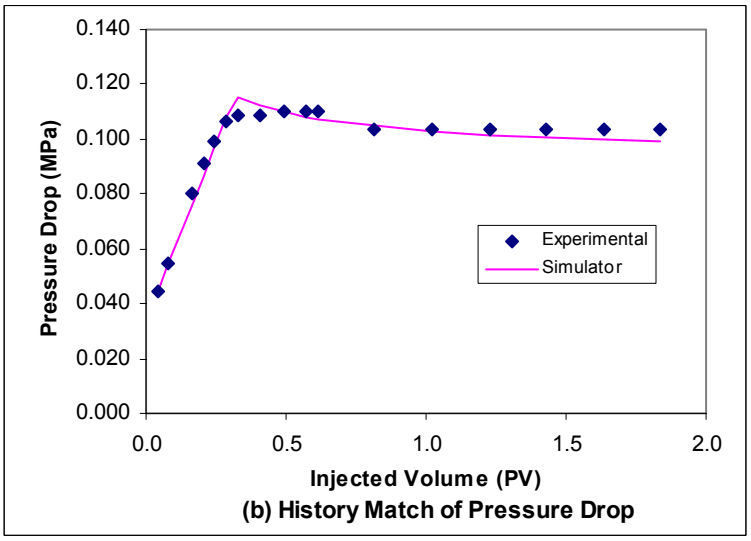


Figure A5: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Nonionic Surfactant Concentration of 5000 ppm





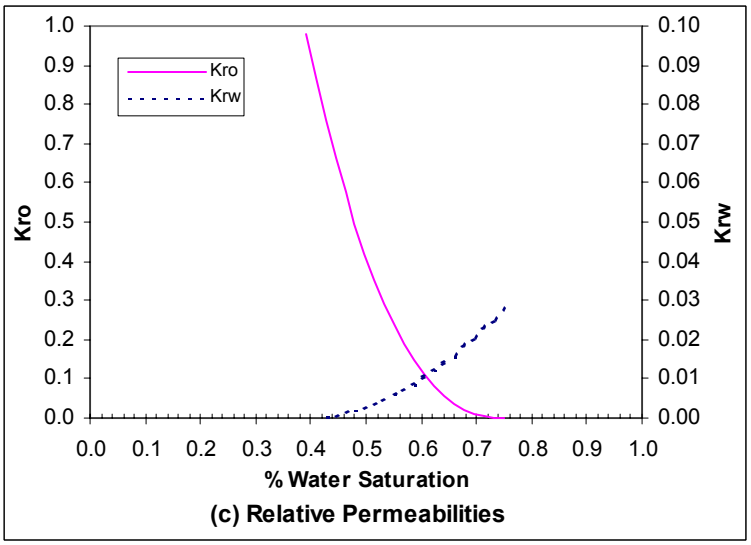


Figure A6: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Nonionic Surfactant Concentration of 0 ppm

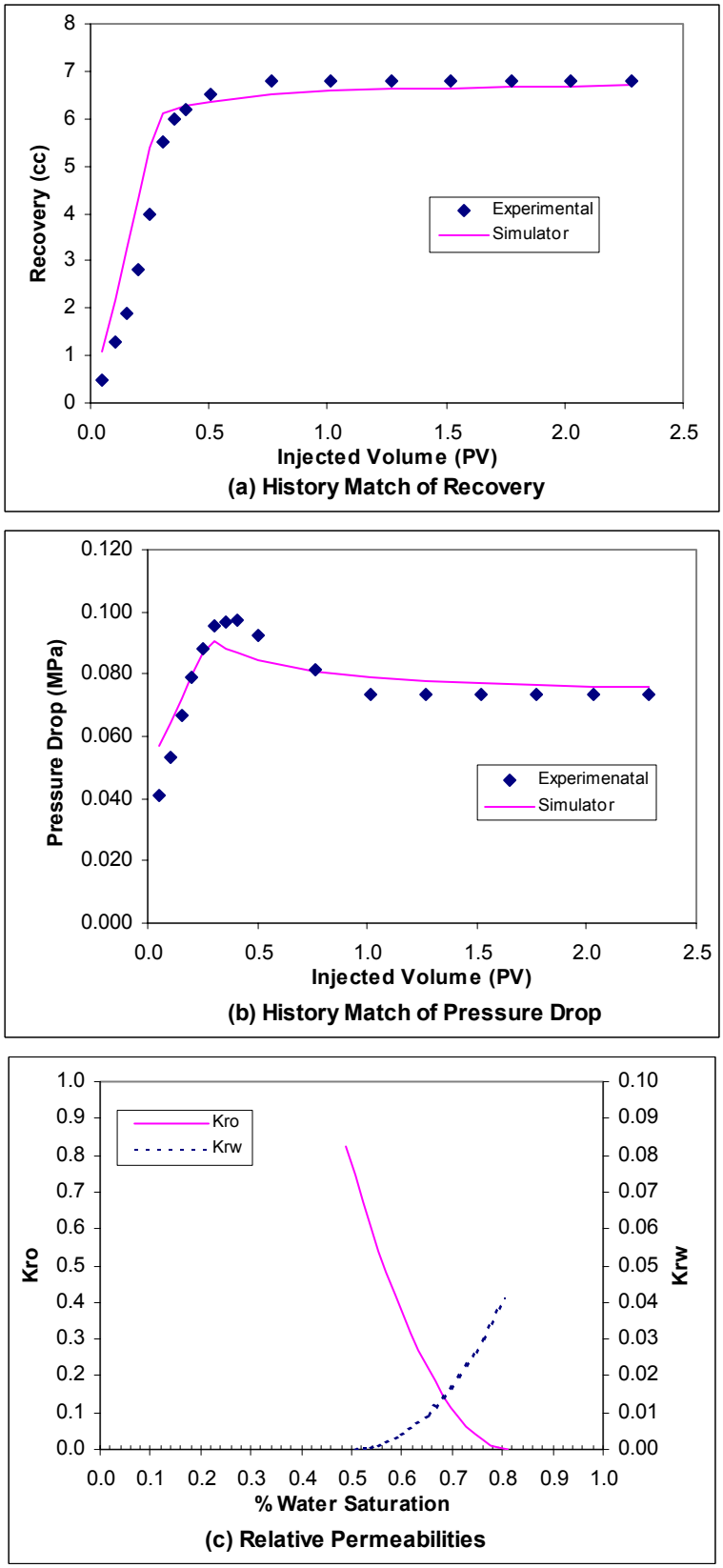
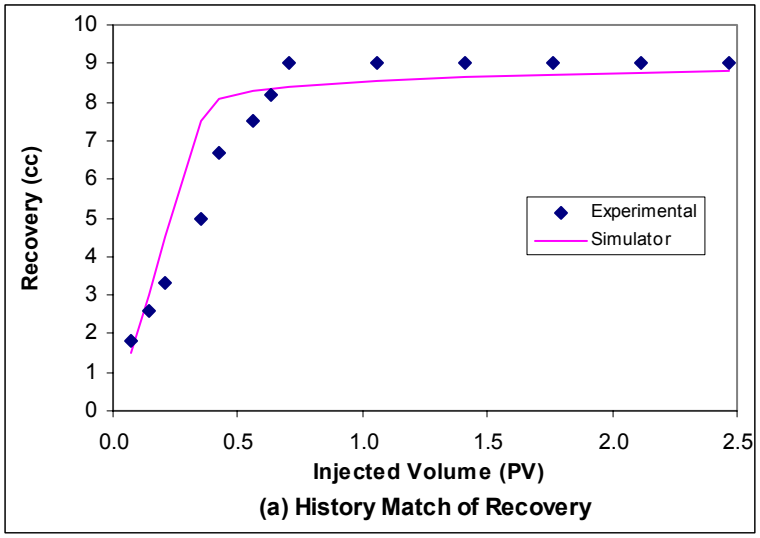
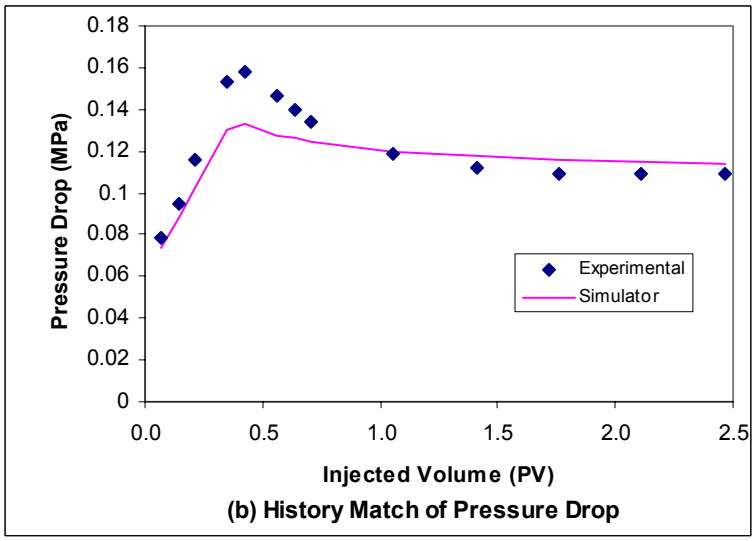


Figure A7: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Nonionic Surfactant Concentration of 500 ppm





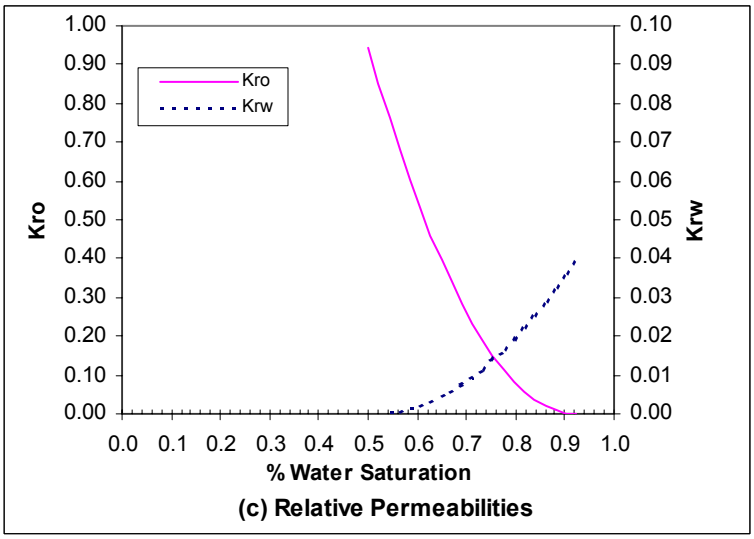


Figure A8: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Nonionic Surfactant Concentration of 1500 ppm

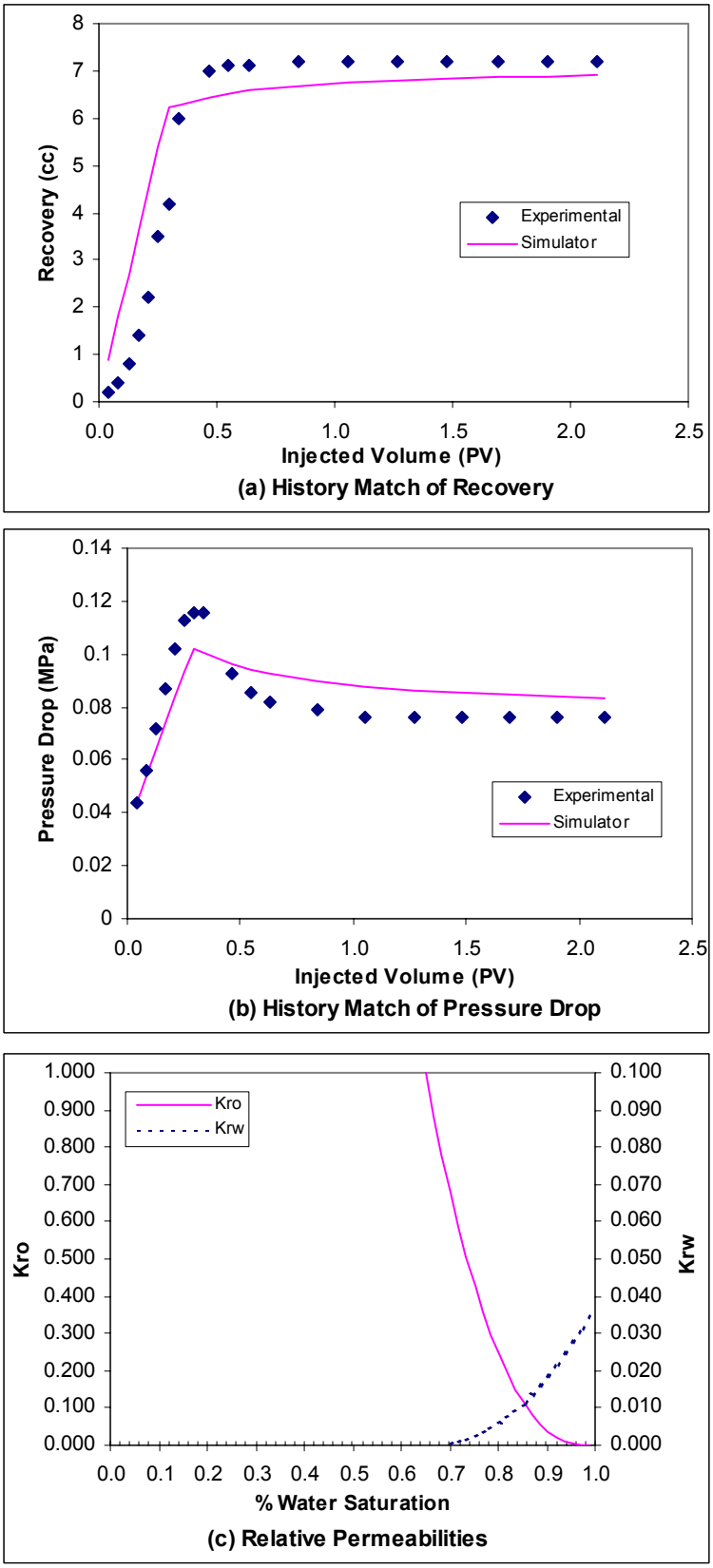
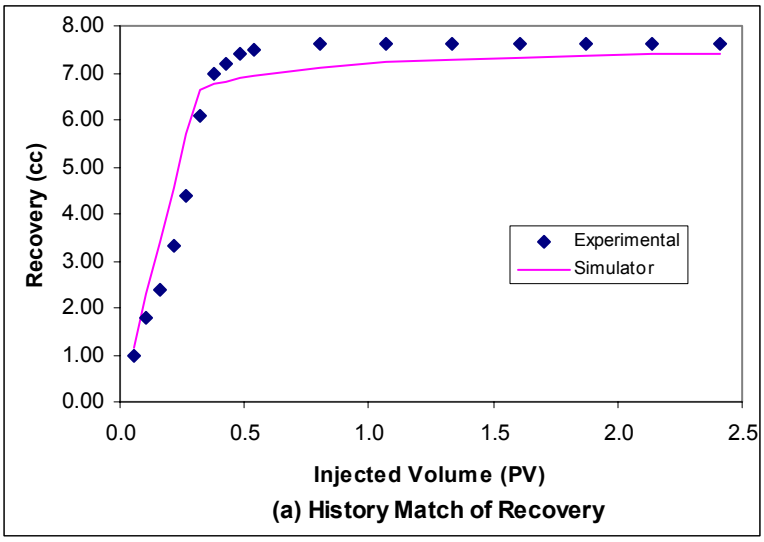
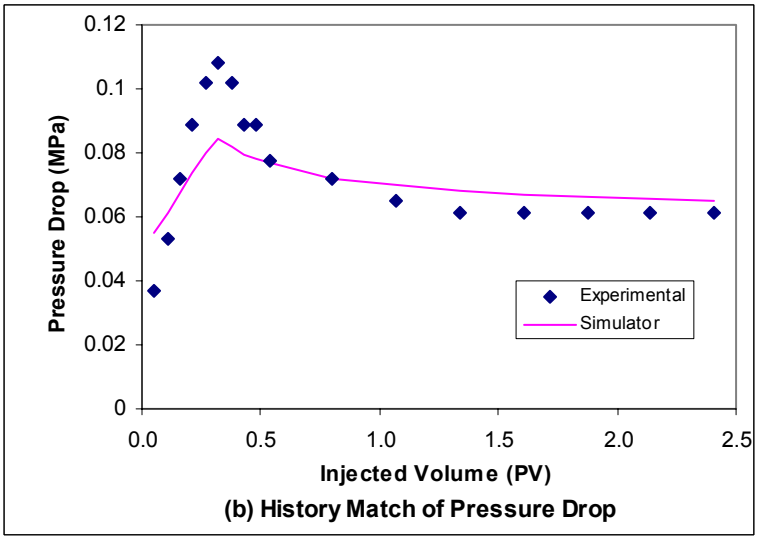


Figure A9: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Nonionic Surfactant Concentration of 3500 ppm





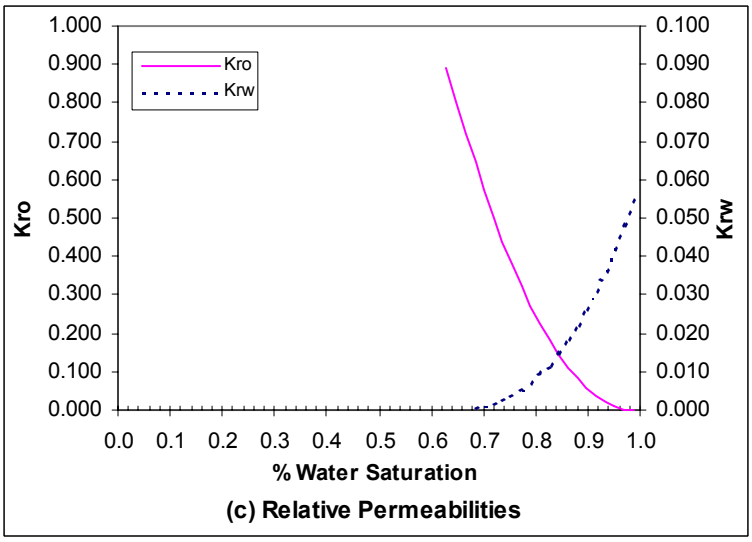
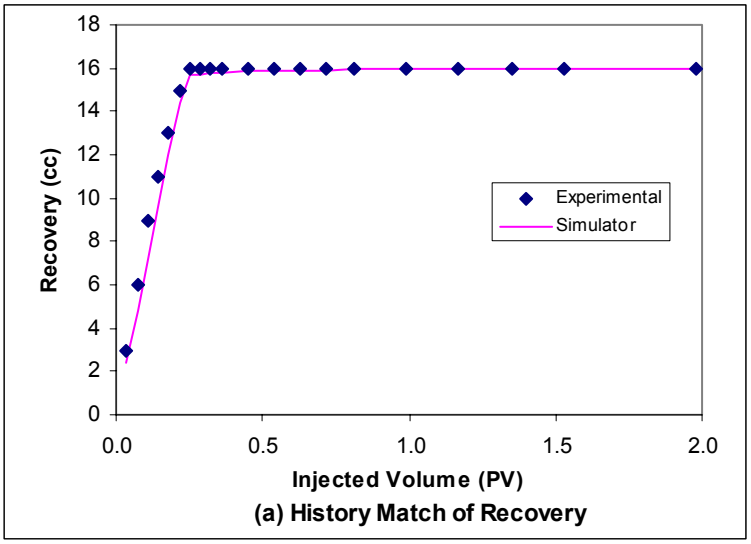
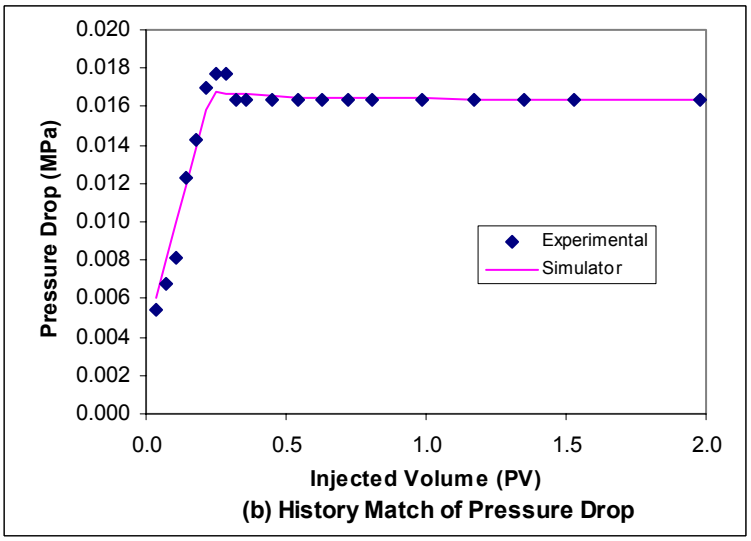


Figure A10: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Nonionic Surfactant Concentration of 5000 ppm





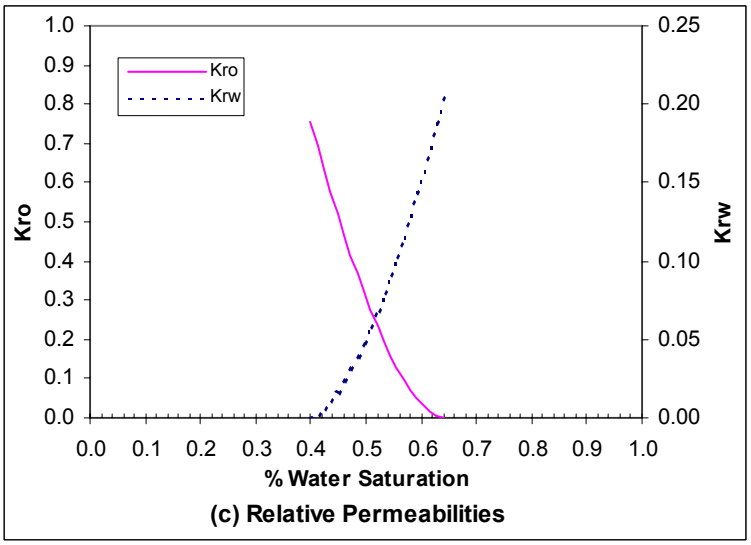
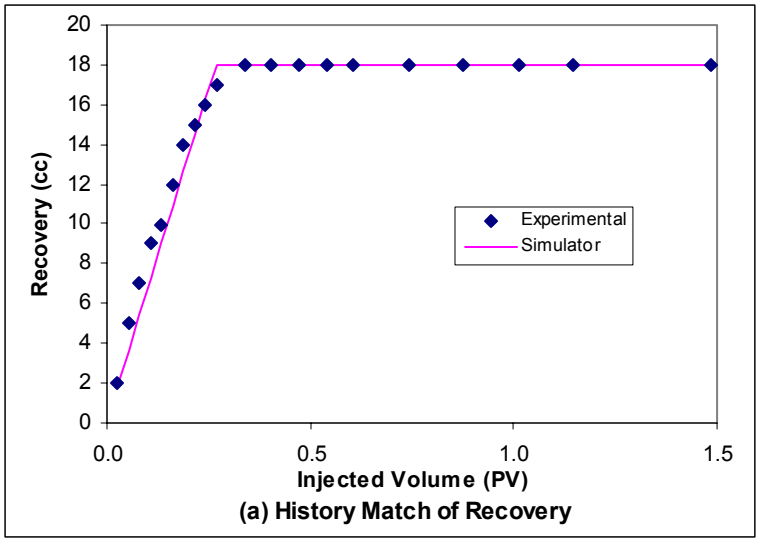
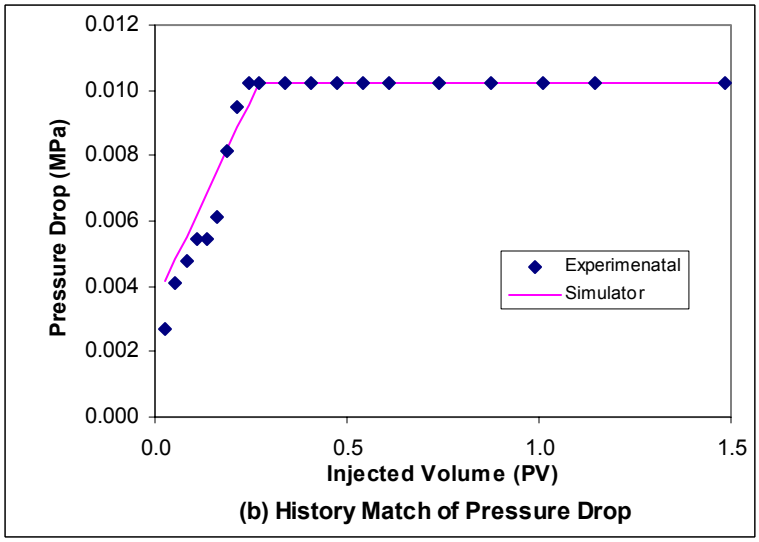
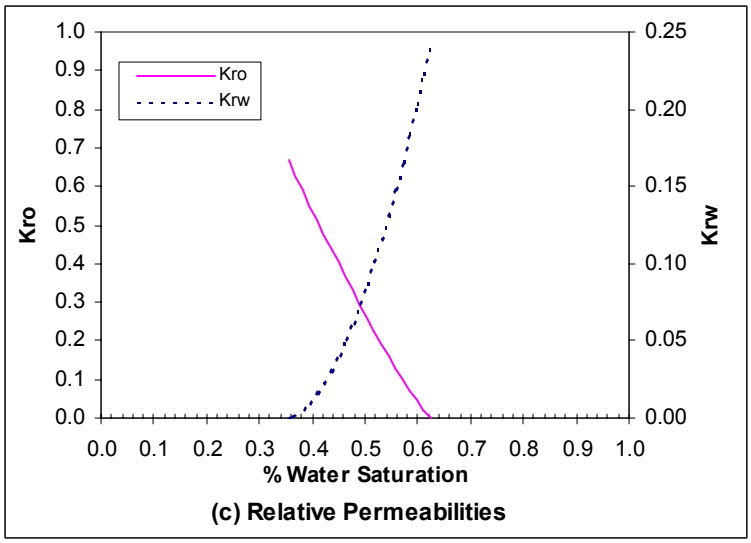


Figure A11: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Anionic Surfactant Concentration of 0 ppm







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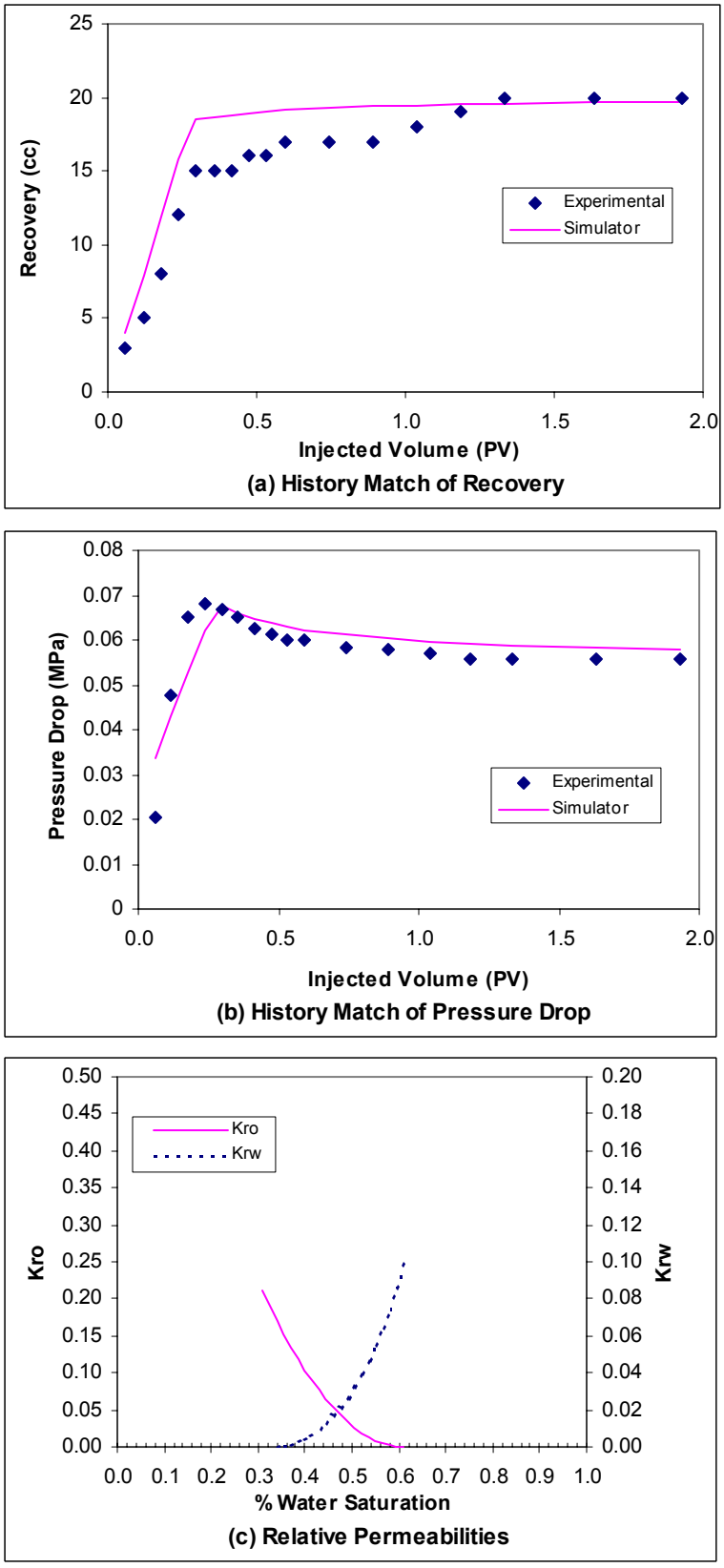
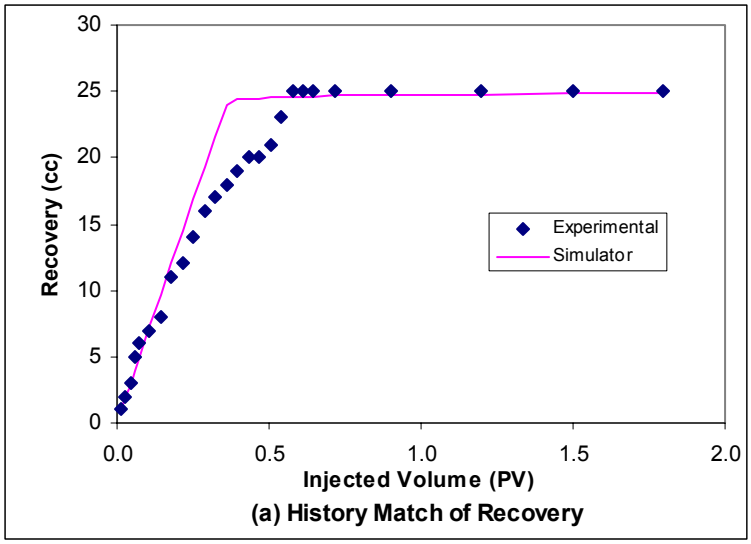
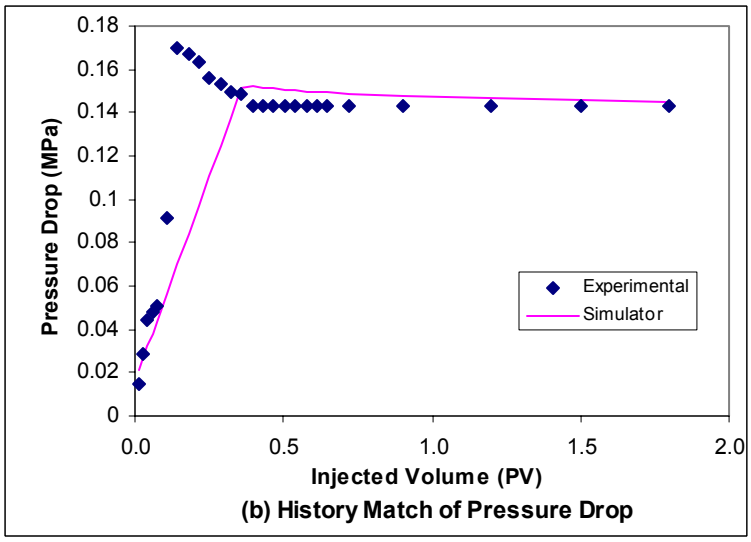


Figure A13: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Anionic Surfactant Concentration of 1500 ppm





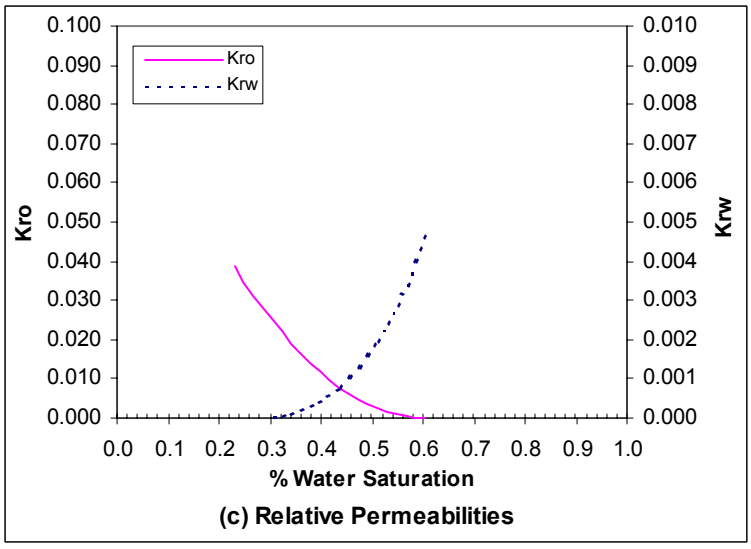


Figure A14: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Anionic Surfactant Concentration of 3500 ppm

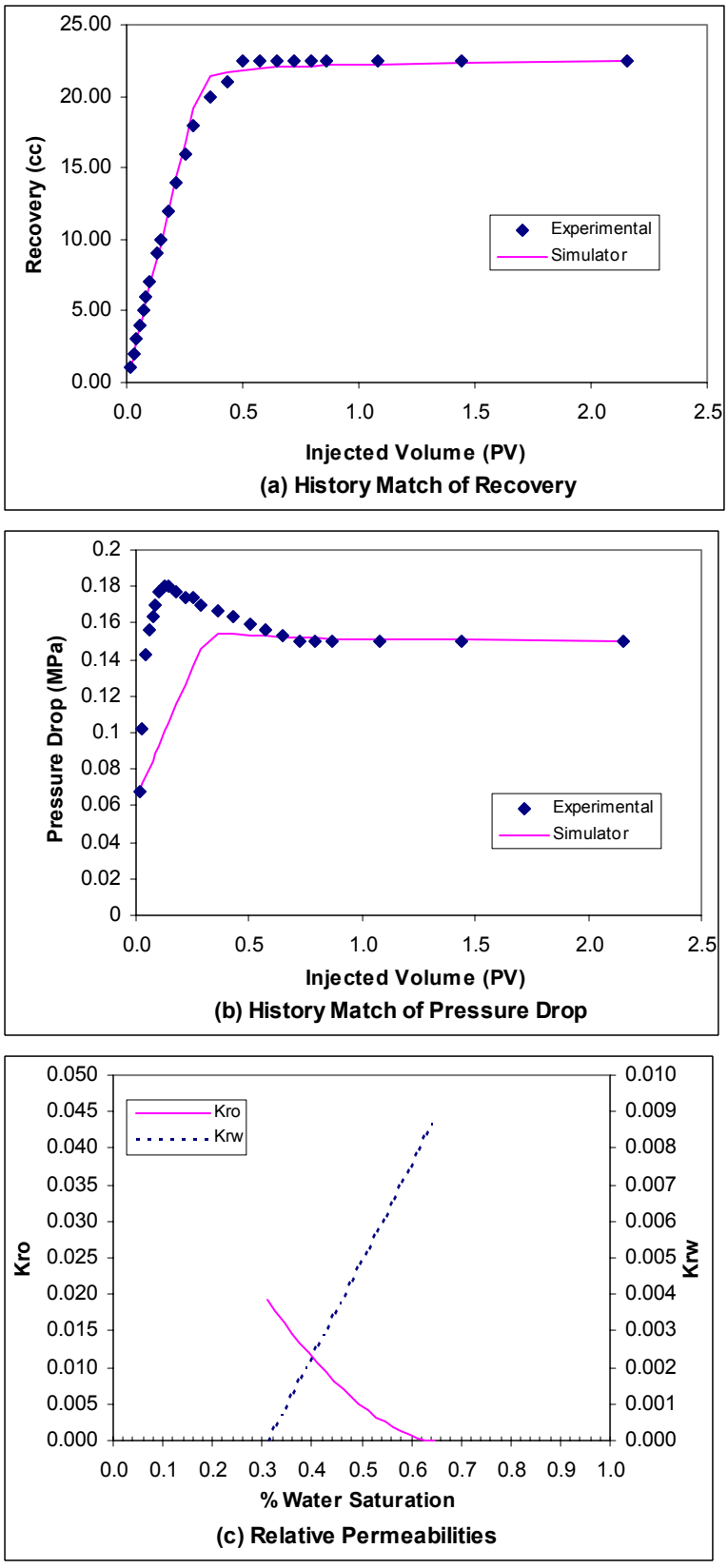
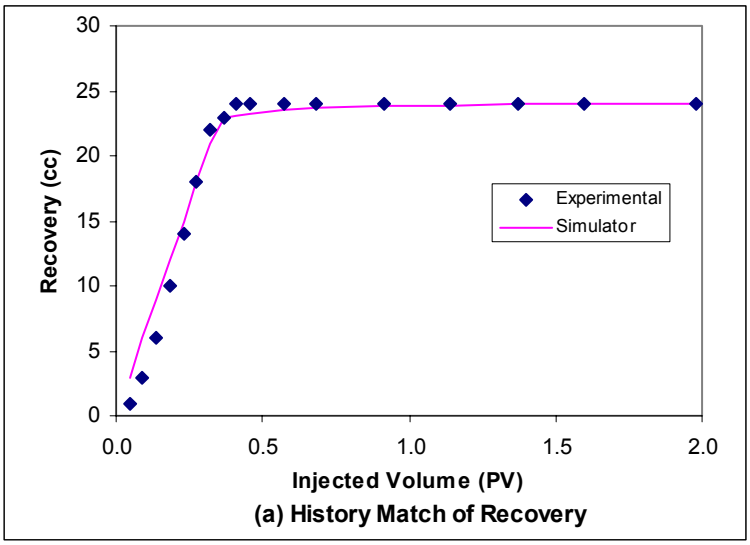
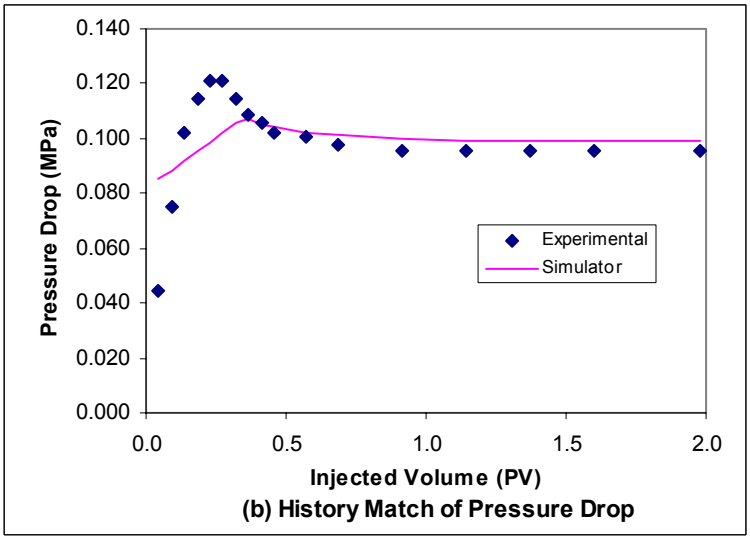


Figure A15: Coreflood Simulator Results for Waterflood of Decane in Berea Core with Anionic Surfactant Concentration of 5000 ppm





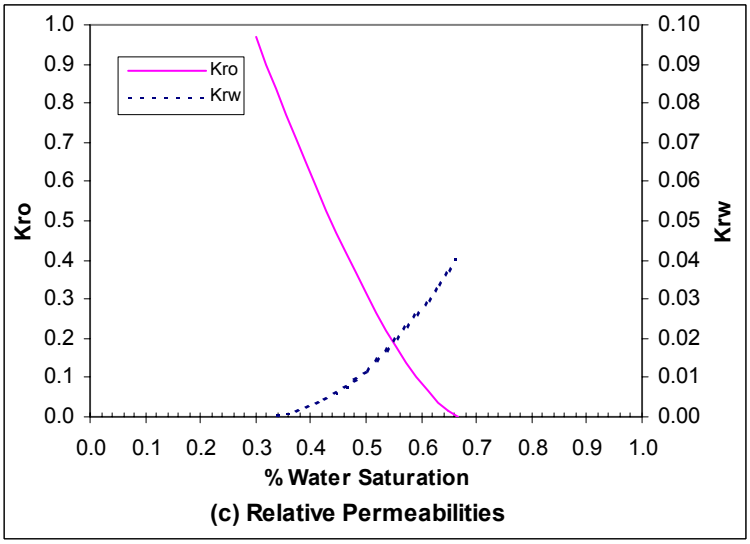
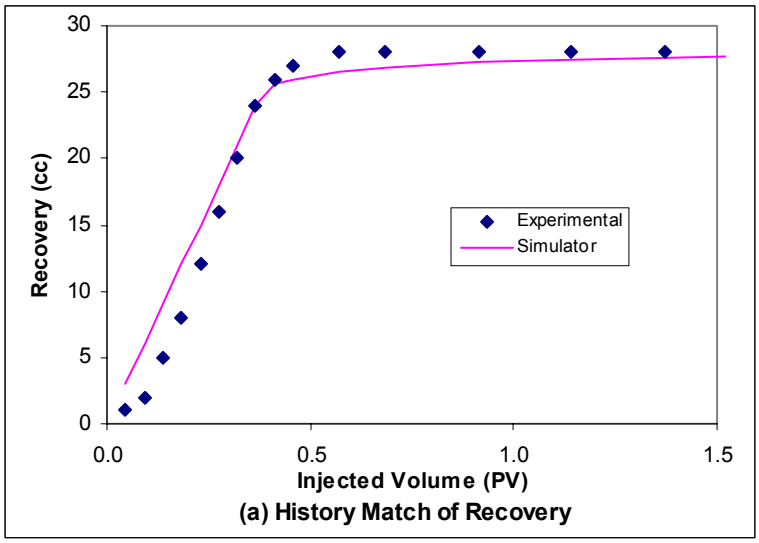
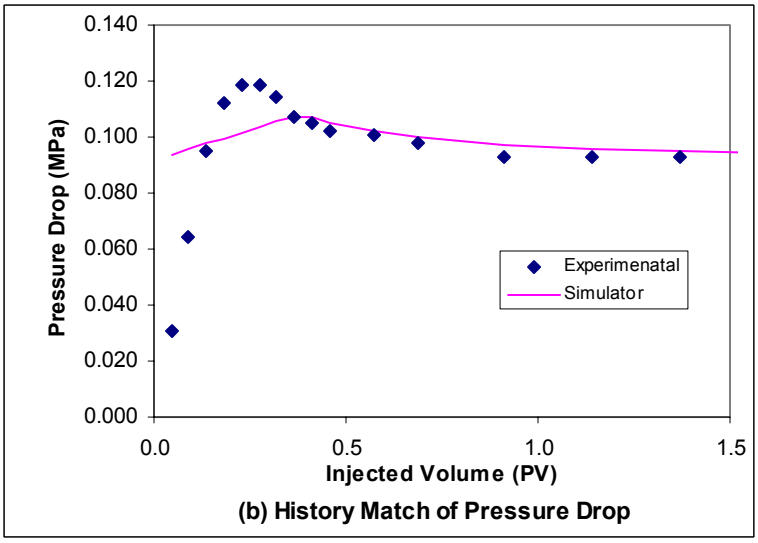


Figure A16: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Anionic Surfactant Concentration of 0 ppm





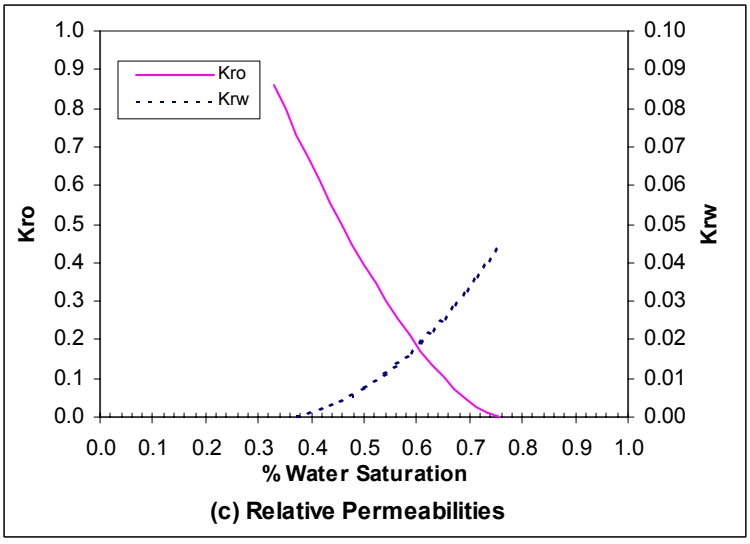
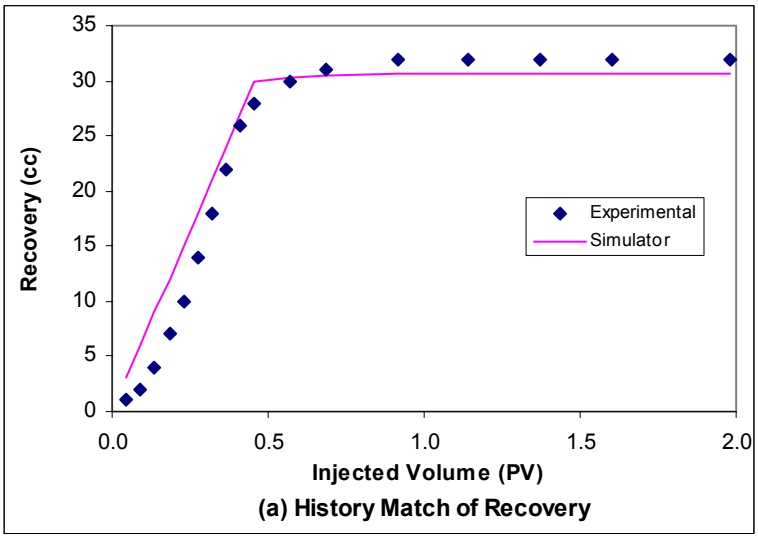
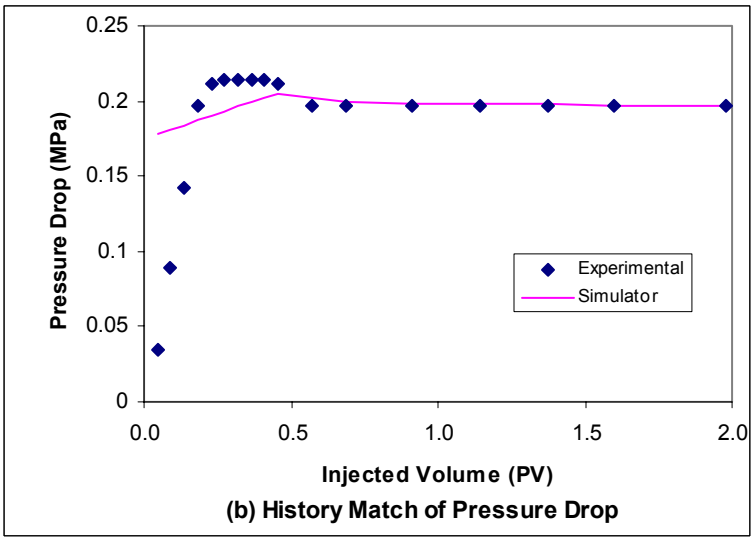


Figure A17: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Anionic Surfactant Concentration of 500 ppm





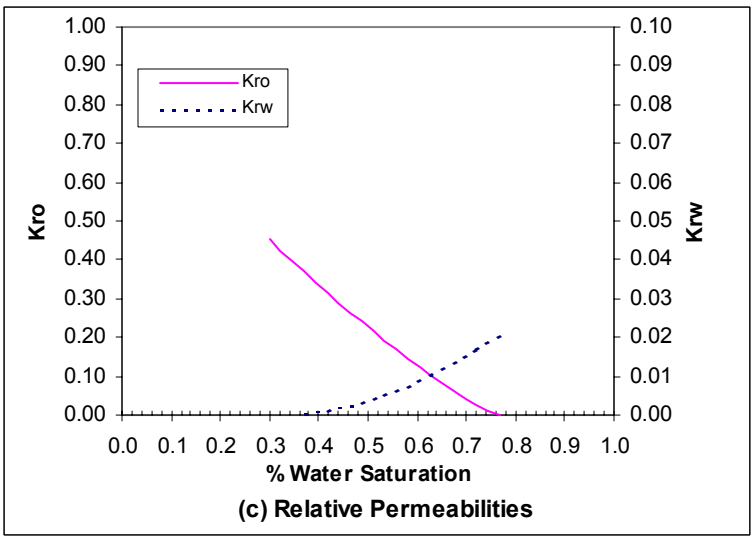


Figure A18: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Anionic Surfactant Concentration of 1500 ppm

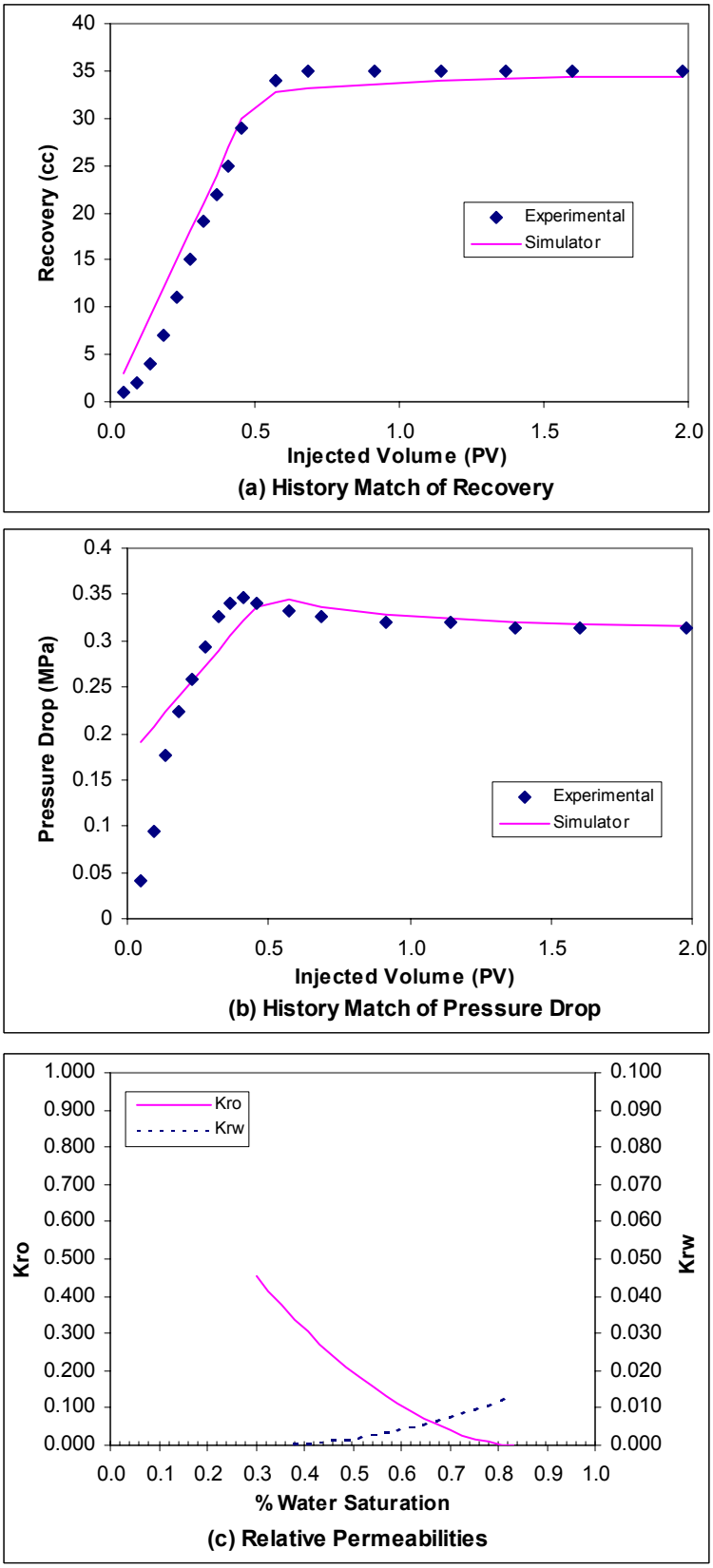


Figure A19: Coreflood Simulator Results for Waterflood of Yates Crude Oil in Berea Core with Anionic Surfactant Concentration of 3500 ppm

VITA

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